THE USE OF POLYURETHANE FOAMS FOR THE EXTRACTION OF PLATINUM(II) FROM HYDROCHLORIC ACID SOLUTIONS IN THE PRESENCE OF TIN(II) CHLORIDE

A thesis submitted to the

UNIVERSITY OF CAPE TOWN

in fulfilment of the requirements for the degree of

MASTER OF SCIENCE

by

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ACKNOWLEDGEMENTS

I would like to take this opportunity to thank

- Dr. Klaus Koch, a patient, conscientious and innovative supervisor whose advice and encouragement have proved to be invaluable during the course of this work,

- Associate Professor Orren, Mrs. Alhadeff, Tony Jutzen and Fred Smith who have helped in many little ways,

- My parents for their past and present support,

- Miss Dreyer for typing this thesis and

- The Council for Mineral Technology (MINTEK) for their generous financial assistance.

A B S T R A C T

ABSTRACT

A preliminary investigation prior to the study of the extraction of platinum, was conducted on the $Co(NCS)_4^{2-}$/foam system to,

(a) develop a suitable experimental apparatus in order to study the loading of platinum foams and

(b) obtain fundamental kinetic and thermodynamic data concerning the sorption process.

The sorption of platinum(II) as complexes of $[Pt(SnCl_3)_nCl_{4-n}]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$ from hydrochloric acid solutions by polyurethane foams was examined in detail. Our studies show that the capacity of the foam to extract platinum depends on the following solution conditions of, temperature, initial platinum concentration, hydrochloric acid and hydrogen ion concentrations, the Sn:Pt ratio and the presence of interfering cations and anions. The rate of platinum sorption is shown to be dependent on temperature, initial platinum concentration, the Sn:Pt ratio and the mass of the foam.

The foam's ability to selectively extract platinum from solutions containing platinum and certain base metals is examined. Results obtained show that in all cases almost complete extraction of platinum was achieved. Of all the base metals investigated only Cu(II) co-extracts to a small extent with the noble metal.

In this work a procedure has been developed in which we are able to quantitatively recover both platinum and tin from loaded foams, by dissolving the polyurethane in warm nitric acid. A simple distillation allows for the satisfactory separation of platinum from tin.

CHAPTER 1

CHAPTER 1

1. INTRODUCTION

The demand for platinum-group metals (PGMs) according to the U.S. Bureau of Mines has increased significantly in recent years[1]. Table 1.1 shows the main consumers of PGMs in the American Economy.

Industry	1970	1973	1976	1979	1980
automotive			21.00	32.68	22.72
chemicals	11.79	17.80	7.40	11.28	8.84
petroleum	6.77	4.47	2.08	6.15	5.31
glass	2.34	2.82	1.52	3.29	1.95
electrical	16.94	20.67	8.90	17.78	16.33
dental and medical	2.10	5.27	5.18	8.43	8.42
jewelry	1.76	1.90	1.19	1.53	2.29
miscellaneous	1.41	4.10	2.52	4.44	3.44
Total	43.11	57.03	49.79	85.58	69.30

TABLE 1.1 U.S. PGM sales in metric tons summarised[1].

The automotive industry which is the principal consumer of PGMs, uses platinum and palladium as oxidation catalysts in the catalytic converters to treat automobile exhaust emissions. Since 1979 rhodium use has increased in the same application as a reduction catalyst for nitrous oxides. Platinum oxidation catalysts are used outside the automobile industry in many pollution abatement processes to remove carbon monoxide and organic vapours.

In the chemical and petrochemical industries the PGMs are again used for their catalytic properties. For example platinum, or a rhodium-platinum alloy, catalyses the partial combustion of ammonia to yield nitric oxide, used

as a raw material for fertilizers, nitric acid and explosives. Platinum catalysts in the petrochemical industry assist in the production of high octane gasoline.

The PGMs have found applications in the glass industry, mostly as containers for molten silicates and in the production of glass fibres. These precious metals also fill a traditional role in the jewelry trade and have continued to be used in greater quantities for dental and medical purposes.

The electrical and electronic industries, which use these noble metals as alloys in low voltage and low energy contacts, thin and thick film circuits and for electrodes, are the third largest consumers of PGMs. Fuel cells in which catalytic platinum electrodes convert fuel directly into electricity, will, if predictions are correct, become a major consumer of platinum in the early 1990s.

In order to satisfy this ever growing demand for the PGMs, use is made of the two principal sources of supply. The smaller of these two is the reprocessing industry which recovers and refines precious metal scrap and spent catalysts. PGMs obtained from this source are termed 'secondary platinum group metals'.

The other supplier of PGMs and the most important one is the mining industry. There are two major types of platinum group ore deposits to be found in the countries of the world's biggest producers, the USSR, South Africa and Canada.

Large igneous ore bodies which are often layered intrusions, containing mafic and ultramafic rocks (rocks in which the gangue minerals are of a low silica content) are the biggest source of PGMs. The major PGM

minerals in these bodies are the sulphides and arsenides, Sperrylite ($PtAs_2$), Cooperite (PtS), and Braggite (Pt, Pd, Ni)S. These minerals are often associated with other sulphides such as copper, nickel and iron and with chromite.

Placer ore deposits in which the precious metals generally occur in their native form, are minor contributors of PGMs to the world market.

The rarity of, and the demand for, these precious metals has resulted in their commanding high prices. The great value attached to the PGMs makes it imperative that the metallurgical recovery of them be as efficient and cost effective as possible. The simplified flow chart in Figure 1.1 summarises the recovery procedure

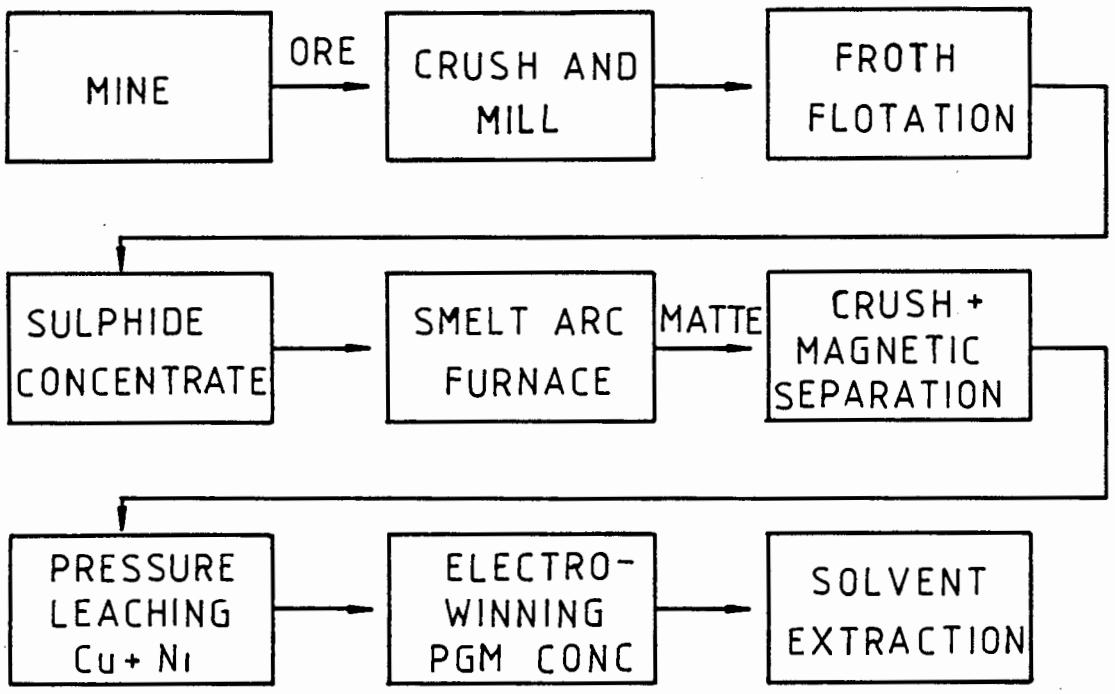


FIGURE 1.1 Flow diagram for the treatment of Platinum ores. Adapted from Kirk-Othmer[1].

The mined ore is crushed and milled to a suitable size and then mixed with water. Suitable hydrophobic organic reagents added to this solution coat the precious metal particles and sulphides, so that when air bubbles are blown through the ore-liquid mixture, these ore particles and sulphides float to the surface as part of the froth. This froth or sulphide concentrate is then smelted in an arc furnace to give a matte, which contains both precious metals and the sulphides of Cu, Ni, Fe and possibly other minor quantities of base metals such as cobalt. Subsequent treatment of the matte by magnetic separation serves to remove the iron sulphide. Pressure leaching removes Cu, Ni and Co and the PGMs are collected by using electrochemical methods. In many processing plants today the actual separation of the PGMs from each other is performed by precipitation and solvent extraction.

1.1 The Sorption of Metals by Polyurethane Foams.

For the past 15 years polyurethane foams have been studied for their use in extracting metals from aqueous solutions. Details of these studies are given later. The advantages of using this solid organic polymer as a metal extractor are numerous. It is cheap, readily available from numerous commercial outlets, has the capacity to hold large quantities of metals, is relatively inert from a chemical point of view and lastly the foam has a physical structure that permits high flow rates of solution through its bulk. The fact that the foam can extract numerous metals under similar conditions is both an advantage and a disadvantage.

1.1.1 Chemical nature of Polyurethane Foams and their formation

Polyurethanes are crosslinked polyether and polyester polymers. The two most important reactions in the formation of polyurethanes are

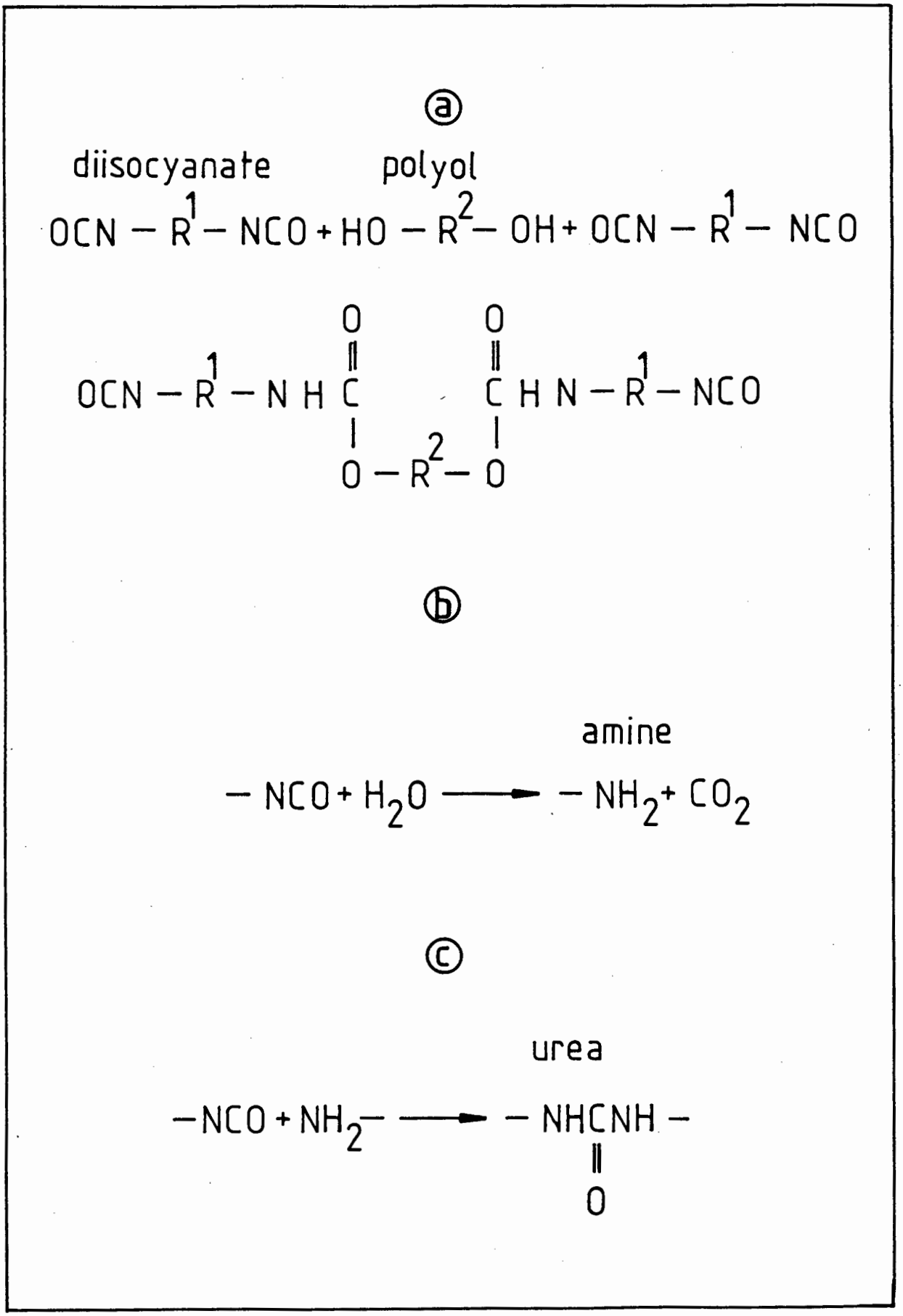


Figure 1.2 Reactions in the formation of polyurethane foams

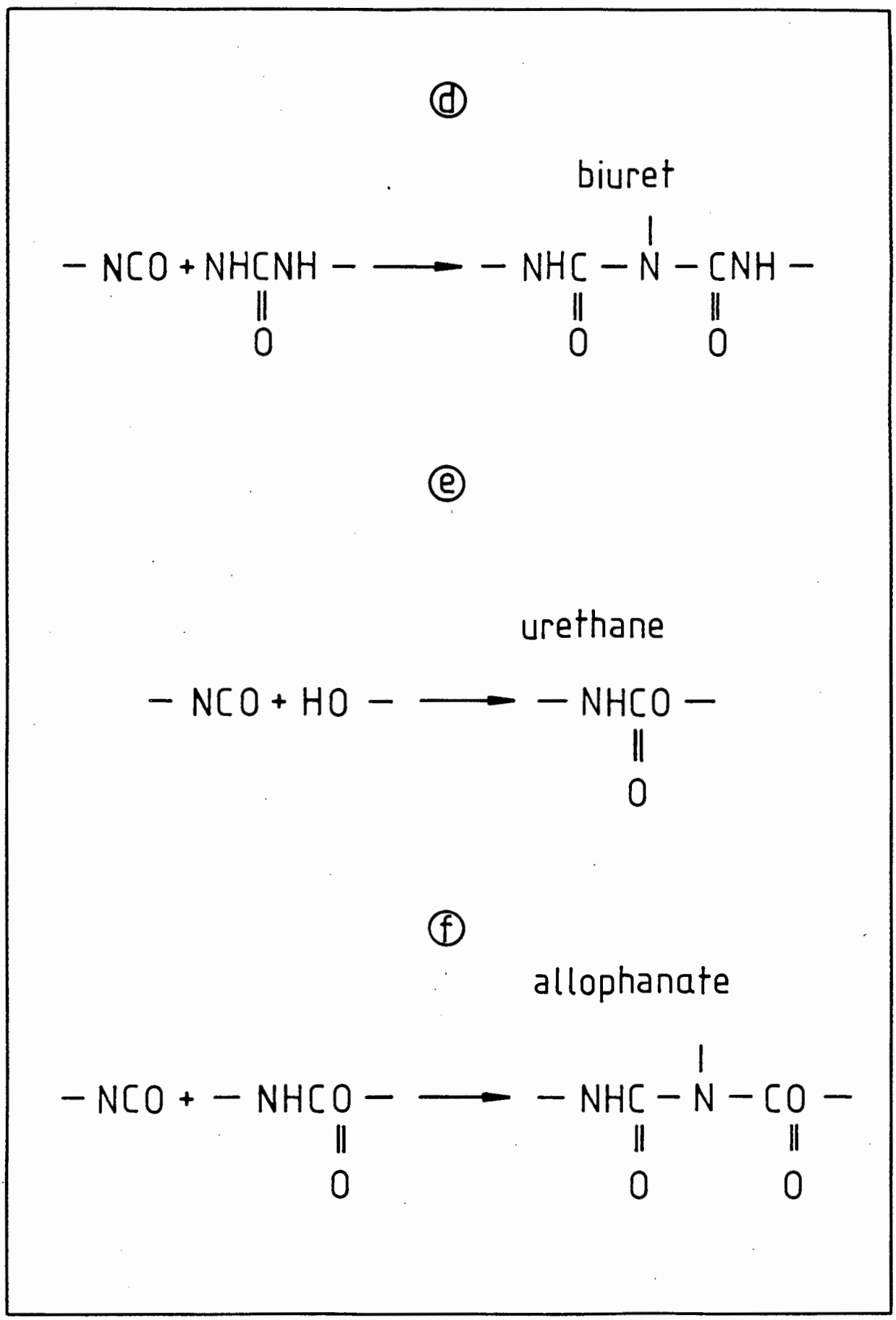


Figure 1.2 Reactions in the formation of polyurethane foams.

those between the isocyanate and hydroxl groups (polyether or polyester polyols) and the reaction between isocyanate and water. Figure 1.2 lists the series of simultaneous reactions that lead to the formation of polyurethane foams. Figure 1.2(a) shows a diisocyanate molecule reacting with a polyol to produce a urethane linked polyether or polyester. In Figure 1.2(b) we see that the isocyanate reacts with water to produce an amine and carbon dioxide. The carbon dioxide produced serves as an *in situ* blowing agent that gives the polymer its foamed structure. Reactions shown in Figure 1.2 (c-f) are side reactions which result in the formation of crosslinks that will influence the final physical properties of the foam.

1.1.2 Historical review of the use of Polyurethane Foams as Extractants and the possible Mechanisms of Sorption

Bowen[2], in a comprehensive study of the sorption of chemical species by polyurethane foams, showed that there were two groups of substances strongly absorbed from aqueous solutions. Free molecules with high polarizability such as iodine, aromatic compounds and metal dithizonates, comprised the one group and univalent anions with high polarizability, such as $AuCl_4^-$, $TlCl_4^-$ and $FeCl_4^-$, which were absorbed to a remarkable extent, the other. Molecules with low polarizability such as nitrogen and n-hexane were not absorbed to any significant extent.

Conclusions drawn by Bowen were;

(a) the capacity of the foam to sorb different metal anionic compounds varied but was of the order of 0.5 - 1.5 moles of metal per kg of foam. Capacities were shown to be temperature dependent.

(b) Desorption of the species from the foam could be achieved easily.

From 1972 to 1974 Braun and Farag[3-5] completed extensive research into reversed-phase partition chromatography. The solid support was the

polyurethane foam onto which a non-polar liquid stationary phase was loaded. A polar liquid mobile phase containing metallic species was then passed over the foam and separations achieved. Braun and Farag[6] also experimented with ion exchange foam chromatography.

It was not until 1977 that any further work was done on the sorption of chemical compounds by unloaded polyurethane foams. Gesser and Horsfall[7] studied the gallium chloride system and came to the conclusion that open cell polyurethane foam behaved as a viscous solvent extractor with a moderate dielectric constant, analogous to diethyl ether. The gallium extracted from acidic aqueous solutions was believed to be in the form $HGaCl_4$. Gesser *et al.*[8] carried out a similar study with the $HFeCl_4$ complex.

Bowen[2] and Hamon[9] considered the possible mechanisms by which polyurethane foams extracted certain chemical compounds. Both authors concurred that absorption rather than adsorbtion processes were responsible for extraction, based on the fact that the capacities of the foam far exceeded surface area measurements of the polymer.

The presence of nitrogen and oxygen atoms in the crosslinks and polyether sections of the foam led Bowen to believe that the polyurethane could behave as a weak-base anion exchanger. In acid solutions these atoms would become positive protonated sites onto which counter anions would move. Hamon concedes that in solutions of low pH the anion exchange mechanism could contribute significantly to the sorption of anionic complexes. He has, however, shown that the extraction of $Co(NCS)_4^{2-}$ into the polyurethane is essentially independent of the hydrogen-ion concentration over a very wide range (pH 1-9).

According to Hamon, the idea of the foam behaving as an ether-like

solvent extractor is sufficient to account for the observed sorption of non-polar, or even moderately polar compounds, but is inadequate when ionic species are involved. It was shown that at high pH values $Co(NCS)_4^{2-}$ is quantitatively sorbed by polyurethane. Under such conditions the complex $H_2Co(NCS)_4$ would not have been present in sufficient quantities to explain the extraction of cobalt in terms of solvent extraction. Distribution ratios of $FeCl_4^-$, $GaCl_4^-$, $Pd(SCN)_4^{2-}$ and $Pt(SCN)_4^{2-}$ in aqueous/polyurethane foam systems ($D=10^4-10^6$ l/kg), are much greater than the distribution ratios measured for those same metal complexes, extracted into liquid organic solvents ($D=10^0-10^1$ l/kg), another fact that argues against a simple solvent extraction type mechanism.

A fourth mechanism considered by Hamon, ligand addition or exchange, involves the donor atoms of the foam, nitrogen and oxygen, complexing the extracted species.

A fifth postulate, known as the cation-chelation mechanism (CCM), was formulated by Hamon and is closely related to the weak-base anion exchange concept. According to the CCM, many cations such as Na^+, K^+, Ag^+, RNH_3^+, Pb^{2+}, Ba^{2+} and H_3O^+ are capable of being multiply complexed, by a helical arrangement of inwardly-directed oxygen atoms belonging to the polyether section of the foam. See Figure 1.3. The polyether spiral engulfs cations completely, much like crown ether compounds[10,11]. Counter anions are simultaneously absorbed along with the cations to satisfy electroneutrality demands and in this respect the CCM differs from the ion exchange mechanism. The extractability of anionic species by polyurethane was shown to be related to their hydrophobicity.

The order of affinity of the polyurethane foams for various cations was shown to be $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ = NH_4^+ < Ag^+ < Tl^+$. This order

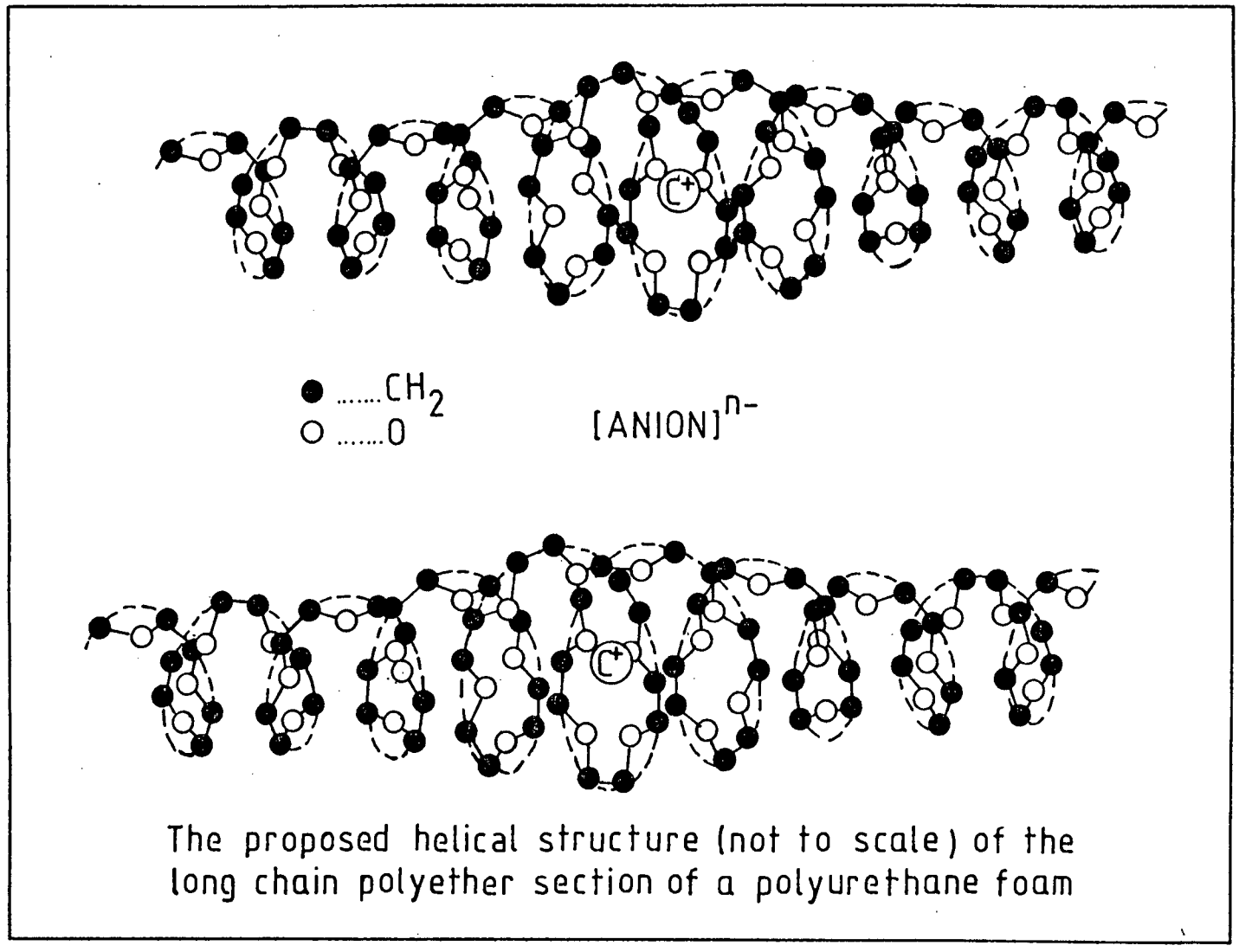


FIGURE 1.3 Metal ion sorption by polyurethane according to the CCM. The Figure is adapted from Hamon's work[9].

almost replicates that shown by 18-crown-6 derivatives.

Work published by Al-Bazi and Chow[12-16] deals with the extraction of the noble metals into polyether polyurethanes as their thiocyanate complexes, e.g. $Rh(SCN)_6^{3-}$, $Pt(SCN)_4^{2-}$ and $Pd(SCN)_4^{2-}$. Foam capacities for these compounds vary but values range from 0.5 - 1.0 moles/kg. The CCM and in certain cases a solvent extraction mechanism, have been used to explain these sorption phenomena.

1.2 Objectives of Research

Stannous chloride in hydrochloric acid media is known to selectively react with PGMs, to form trichlorostannato anionic complexes. A preliminary study by Nel[17] at the University of Cape Town has shown that polyurethane foams extract platinum from solutions containing tin(II) chloride. This potentially selective method of extraction, which could improve the performance of today's established metallurgical treatments of the PGMs, led to the formulation of a series of objectives summarised here.

(a) With a view to studying conditions for the platinum extraction in detail, we investigated how the following factors might effect the capacity of the foam for these anionic complexes and how some of these factors effect the rates of sorption.

(i) Temperature

(ii) Initial concentration of platinum in solution

(iii) Sn:Pt molar ratio of the initial solution

(iv) Hydrochloric acid concentration of the solution

(v) Hydrogen ion concentration of the solution

(vi) The presence of certain alkali-earth cations (Li^+, Na^+ and K^+) in solution

(vii) The presence of certain anions in solution

(viii) Different masses of foam

(b) To study how selective the polyurethane foams are in extracting platinum in the presence of other base metals.

(c) To evaluate a means of recovering platinum and tin from loaded foams and separating the two.

1.3 The Platinum-Stannous Chloride Complexes

Wöhler[18] first reported that when dilute HCl solutions of $PtCl_4^{2-}/PtCl_6^{2-}$ and $SnCl_2$ were mixed, that a solution with an intense red colour resulted. Wöhler and Spengel[19] suggested the red colour was due to colloidal platinum produced in the reaction between Pt(IV) and Sn(II). This postulate was disproved by Ayres and Meyer[20] who showed that the coloured material readily passed through a semi-permeable membrane. Further evidence against platinum existing in a colloidal form is the fact that the red colour is extractable into organic solvents.

The red colour of the platinum-tin chloride complexes has also been attributed to chloroplatinous acid[21,22] and to platinum(II)[23].

Today the generally accepted oxidation state for platinum in the Pt-Sn complexes is 2. Ayres and Meyer, however, based on the fact that tin(IV) has been found in solutions of $PtCl_4^{2-}/PtCl_6^{2-}$ and stannous chloride, contend that the platinum is in a zero valence state[24]. Potentiometric and polarographic studies by Elizarova and Matvienko[25] on the same chemical system came to the same conclusion as Ayres and Meyer.

Spectrophotometric studies of the Pt-Sn complexes in aqueous solution by Ayres and Meyer[24], showed that stannous chloride can bond to platinum in the following molar ratios (Sn:Pt), 1:4, 1:2, 1:1, 3:2, 2:1, 3:1 and 5:1, with the principal complex being 5:1.

Precipitation tests by Ayres and Meyer indicated the existence of a

tetrapositive cationic complex containing Pt(0) and Sn(II) chloride, to which the formula $[PtSn_4Cl_4]^{4+}$ was given. This formulation is largely discounted today.

Electrophoresis studies by Shukla[26] showed the presence of anions when platinum and stannous chloride solutions were mixed. Young and co-workers[27] confirmed the existence of anionic complexes when they managed to precipitate out of solution the proposed *cis* and *trans* forms of $[PtCl_2(SnCl_3)_2]^{2-}$ with tetramethylammonium salts. Young *et al.* showed that the *cis* and *trans* forms (Figure 1.4(a)) which were thought to be yellow and red respectively, existed in solutions in which the Sn:Pt ratio was low. Solutions containing Sn:Pt molar ratios greater than 2:1 yielded red salts which frequently contained more than 2 moles of tin per mole of platinum.

The quinqueco-ordinated ion $[Pt(SnCl_3)_5]^{3-}$ identified by X-ray diffraction studies[28] and shown in Figure 1.4(b), is thought to predominate in solutions with a high Sn:Pt ratio. The configuration of $[Pt(SnCl_3)_5]^{3-}$ has been shown to be trigonal bipyramid consisting of a central platinum atom surrounded by five $SnCl_3^-$ ligands attached through platinum-tin bonds[28]. The trichlorostannato ion with its lone pair of electrons behaves as a weak σ-donor and in accepting electrons via back bonding with the platinum behaves as a strong π acceptor[29].

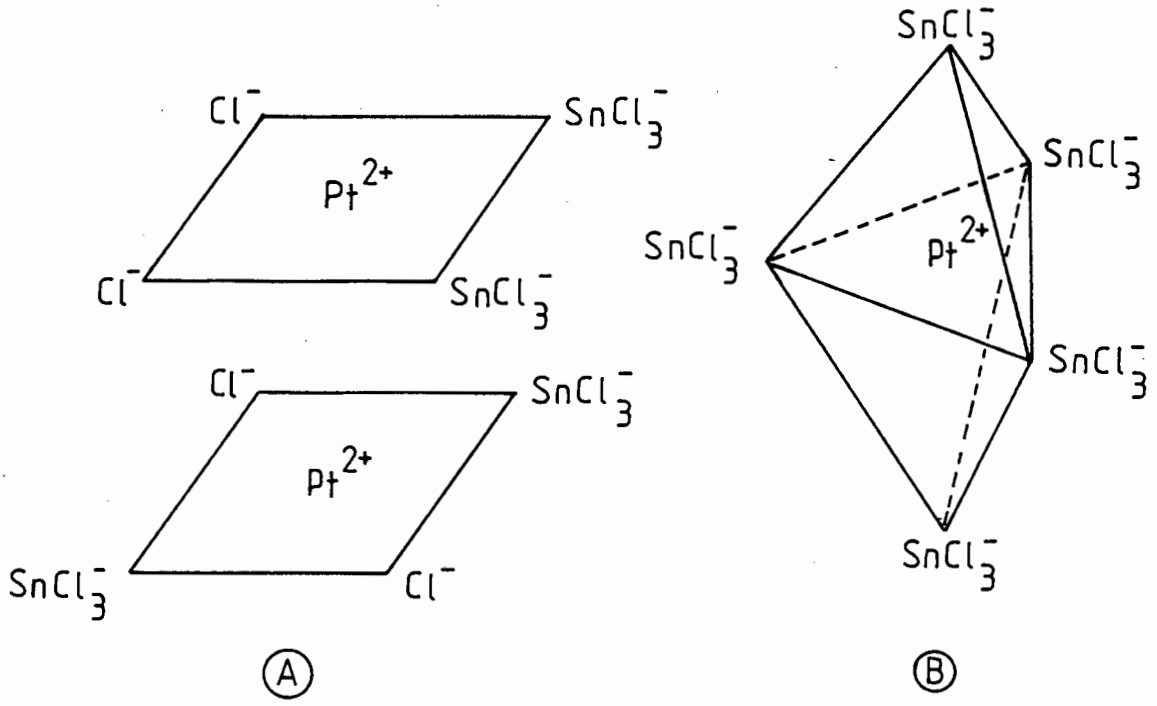


Figure 1.4 (a) *Cis* and *trans* $[PtCl_2(SnCl_3)_2]^{2-}$ (b) $[Pt(SnCl_3)_5]^{3-}$

Young*et al.*[27] proposed the following equilibria existed simultaneously in solutions containing tin(II) chloride and platinum(II) chloride.

$$SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-$$

$$[PtCl_4]^{2-} + SnCl_3^- \rightleftharpoons [PtCl_3(SnCl_3)]^{2-} + Cl^-$$

$$[PtCl_3(SnCl_3)]^{2-} + SnCl_3^- \rightleftharpoons \textit{trans}\text{-}[PtCl_2(SnCl_3)_2]^{2-} + Cl^-$$

$$\textit{trans}\text{-}[PtCl_2(SnCl_3)_2]^{2-} \rightleftharpoons \textit{cis}\text{-}[PtCl_2(SnCl_3)_2]^{2-}$$

$$\textit{cis}\text{- and } \textit{trans}\text{-}[PtCl_2(SnCl_3)_2]^{2-} + 3SnCl_3^- \rightleftharpoons [Pt(SnCl_3)_5]^{3-} + 2Cl^-$$

In more recent years the existence of the *trans* form of $[PtCl_2(SnCl_3)_2]^{2-}$ has been questioned following the results of a Mössbauer study[30]. Mössbauer spectra of the supposed *trans* complex yielded the same spectra as the red anion $[Pt(SnCl_3)_5]^{3-}$. Furthermore in 1980 a multinuclear NMR study questioned the existence of the red form of $[PtCl_2(SnCl_3)_2]^{2-}$ [31]. The supposed red isomer isolated from a 3M HCl solution of tin and platinum chloride appeared to be a mixture of the red

$[Pt(SnCl_3)_5]^{3-}$ and the yellow $[PtCl_2(SnCl_3)_2]^{2-}$ complexes.

1.4 Definition of Terms used

1.4.1 The Capacity of the foam

The maximum quantity of a metal that a certain mass of foam can accommodate is defined here as its capacity;

$$C_m = \frac{\text{moles of metal extracted by foam}}{\text{mass of foam (kg)}}$$

where C_m is the capacity of the foam to sorb the metal (m).

1.4.2 The Distribution Ratio

The commonly used distribution ratio in polyurethane studies is;

$$D = \frac{\text{\% metal on foam}}{\text{wt of foam (g)}} \quad X \quad \frac{\text{wt of solution}}{\text{\% metal left in solution}}$$

1.4.3 The Mass Distribution Ratio

The mass distribution ratio was introduced in this work, so that the reader could readily appreciate the extent to which different masses of polyurethane foams extract certain anionic metal complexes. The mass distribution ratio D_m is defined here as;

$$D_m = \frac{\text{mass of metal (mg) sorbed by foam}}{\text{mass of foam (mg)}}$$

1.4.4 The Sn:Pt ratio of a solution

For the sake of brevity the term R_a is introduced to denote the Sn:Pt molar ratio of the solution.

1.4.5 The Sn:Pt ratio of species in the foam

R_f denotes the average Sn:Pt molar ratio of species sorbed into the polyurethane foam.

CHAPTER 2

2. METHODS OF ANALYSIS

A study of the extraction of platinum as its stannous chloride complexes from dilute HCl solutions, into polyurethane foams, requires analysing solutions for both platinum and tin. The conventional gravimetric and colorimetric methods of determining the noble metals are often time consuming and tedious. These traditional methods of analysis of the platinum group metals have been largely replaced by Atomic Absorption Spectroscopy (AAS), a very popular analytical technique used in the analysis of over 60 elements[33].

2.1 Atomic Absorption Determination of Platinum

Depressive inter-element interferences can be a problem in the assaying of noble metals by AAS. These serious interferences were first noted by Strasheim *et al.*[34] in his determination of platinum and rhodium in the presence of other noble and base metals. To prevent inter-element interferences one can either use hotter flames and/or suitable releasing agents.

To remedy the problem of mutual interferences (interferences caused by other noble metals) Strasheim added a variety of base metals to the analyte solutions. He found that $CuSO_4$ and $Cu(NO_3)_2$ at the 20,000 p.p.m. level overcame the reduction in the platinum absorption readings. The disadvantage of using these high concentrations of copper salts is that it leads to the burner head clogging.

Schnepfe and Grimaldi[35], in the determination of palladium and platinum found that mutual and base metal interferences were removed by the addition of a mixture of copper and cadmium sulphates.

Mallett *et al.*[36] investigated the following releasing agents; lanthanum, copper sulphate, copper+cadmium sulphate, uranium and vanadium and found they were effective in removing mutual interferences for one or more of the noble metals in the air-acetylene flame. Vanadium was found to remove mutual and base-metal interferences.

A 0.5% lithium sulphate buffer in an air-acetylene flame was shown by Pannetier and Toffoli[37] to both enhance the sensitivities of platinum, rhodium and iridium and eliminate inter-element interferences in the determination of these elements and palladium.

Vasilyeva *et al.*[38] in a study of the noble metals, investigated many of the additives used by Mallett *et al.* as well as the following; $LaCl_3$, $La(NO_3)_3$ $La_2(SO_4)_3$, $NdCl_3$, $Nd(NO_3)_3$ and $Nd_2(SO_4)_3$. Of these releasing agents only $La(NO_3)_3$ and $Nd(NO_3)_3$ successfully lowered the limit of detection of Pt, Rh, Ir and Ru and inhibited the effect of Co, Cu, Ni, Fe, Bi, Zn and Na on their determinations. Lanthanum and neodymium chlorides and sulphates produced a similar effect but only on the determination of Pt and Rh.

Three types of flame have been used for assaying the noble metals by AAS. The earlier investigators[34] used the cool butane-propane-air flame. Two other alternative flames are the more commonly used air-acetylene one or the nitrous oxide-acetylene version.

In deciding upon AAS parameters to operate under for our study of platinum, the following considerations were taken into account. Although the hotter nitrous oxide-acetylene flame reduces inter-element interferences, it also reduces the sensitivity of the platinum due to the increased ionization of the analyte at higher temperatures. For this reason we chose the cooler air-acetylene flame and relied upon a releasing agent to remove inter-element interferences.

Our choice of $La(NO_3)_3$ as a releasing agent was based on the work of Vasilyeva[38]. Although mutual interferences were not a problem in our experimental solutions, (platinum being the only noble metal present) the presence of $La(NO_3)_3$ served to enhance the platinum absorbance readings. For the solutions containing base metals the $La(NO_3)_3$ inhibited the interference of these elements.

The platinum resonance line at 265.9 nm was chosen in this study for its sensitivity. For the platinum concentration range in which analysis was done (0-50 ppm) Beer's Law was obeyed. The standards used contained K_2PtCl_4, 0.2% $La(NO_3)_3$ and tin(II) chloride. A standard calibration curve for platinum is shown in Figure 2.1.

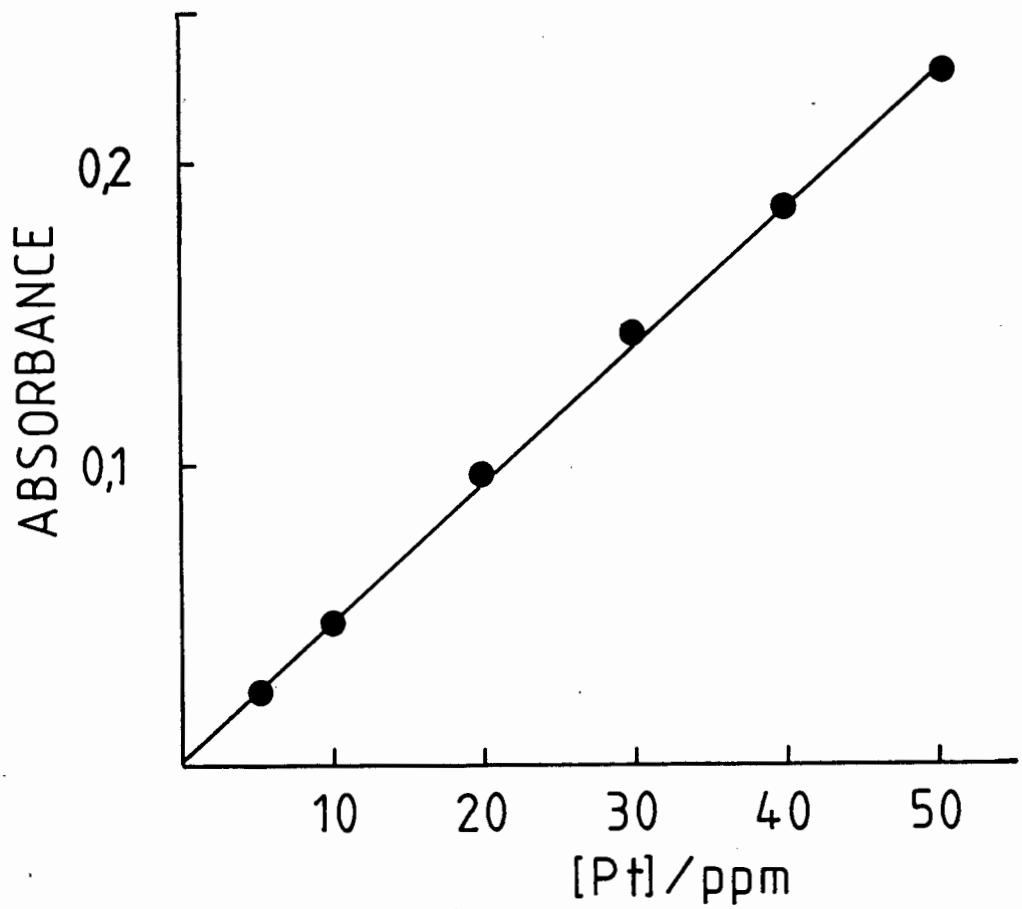


Figure 2.1 A calibration curve for platinum in 1.0M HCl and 0.2% $La(NO_3)_3$ and stannous chloride Sn:Pt = 2.

Throughout this work we attempted to match standards and samples as closely as possible. This was done in view of work reported by Yates[39], who showed that more accurate results were obtained for platinum if standards were made up containing tin(II) in approximately the same concentration as the sample.

2.2 Atomic Absorption Determination of Tin

The determination of tin in aqueous hydrochloric acid media by AAS is relatively simple[40]. Numerous different flames have been used and these include, air-acetylene, argon-hydrogen, nitrous oxide-acetylene and nitrogen-hydrogen-entrained air.

The strongly reducing air-acetylene flame, was chosen for our tin assaying despite its lower sensitivity compared to other flames[41]. The air-acetylene flame does have the advantage of being less subject to interferences than either the nitrous oxide-acetylene or the air-hydrogen flames.

The absorbance readings were recorded at a wavelength of 286.3 nm. Table 2.1 confirms the findings of Yates[39] that platinum does not interfere in the determination of tin. Table 2.2, in agreement with Wyrley-Birch's work[42], shows that the higher the HCl concentration of a solution, the lower is the tin absorbance. It is therefore necessary to match standards and samples with respect to their HCl concentrations. A standard tin calibration curve is shown in Figure 2.2

Sn:Pt ratio	[Sn] taken/ ppm	[Sn] found/ ppm	Relative Percentage Error
1:1	100.0	100,5	0.5
1:1	50.0	49.5	0.5
1:2	100.0	100.0	0.0
1:2	50.0	51.0	1.0
1:5	100.0	99.0	1.0
1:5	50.0	50.0	0.0

Table 2.1 The effect of platinum on the determination of tin in 1.0M HCl

[Sn]/ppm	[HCl]/M	Absorbance
100	1.0	0.167
	2.0	0.165
	3.0	0.162
	4.0	0.160
50	1.0	0.115
	2.0	0.114
	3.0	0.112
	4.0	0.111

Table 2.2 The effect of [HCl] on the tin absorbance signal.

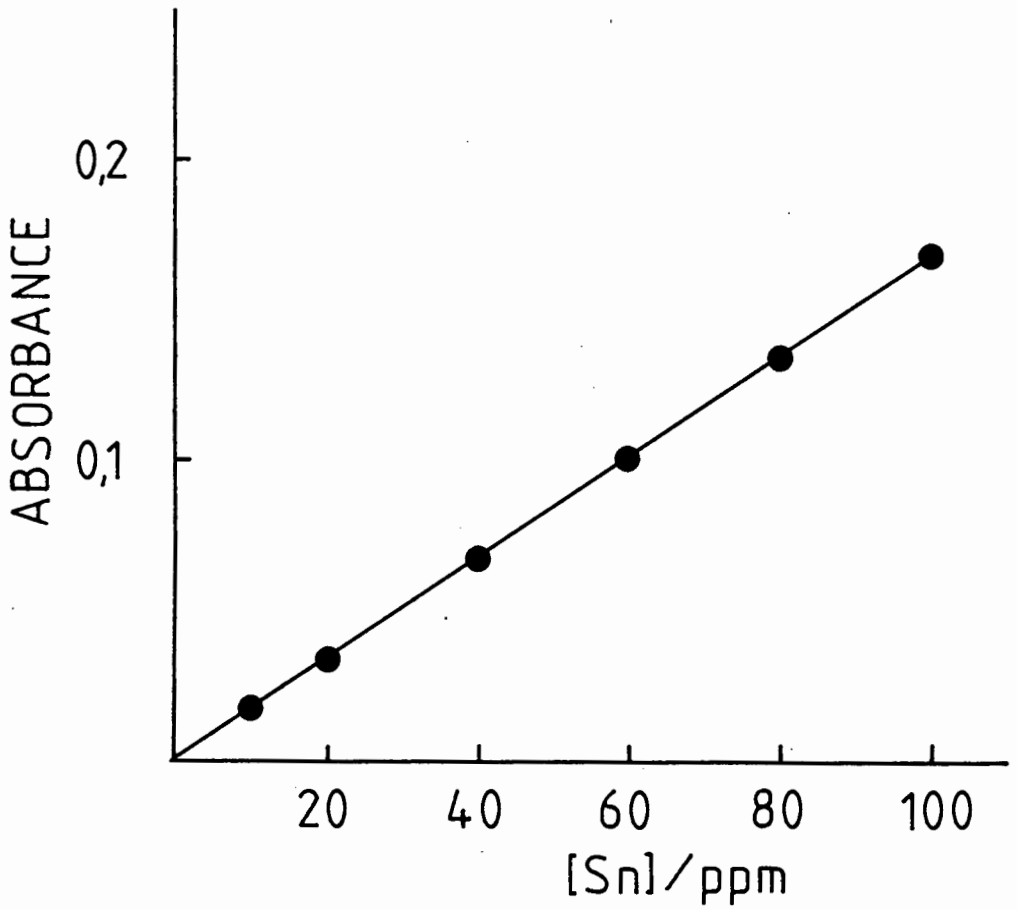


Figure 2.2 Calibration curve for tin in 1.0M HCl

2.3 Atomic Absorption Determination of the base metals

The base metals, Fe, Co, Ni, Cu and Zn in dilute hydrochloric acid solutions are readily determined by AAS. The conditions under which they are analysed are to be found in Table 2.3.

Base Metal	Flame Type	Absorption Wavelength	Burner-Head Configuration
Fe	Air-Acetylene	372.0	normal
Co	Air-Acetylene	304.4	normal
Ni	Air-Acetylene	232.0	rotated 90°
Cu	Air-Acetylene	324.7	rotated 90°
Zn	Air-Acetylene	213.9	rotated 90°

Table 2.3 AAS conditions for assaying the base metals.

According to the Varian Techtron 70 manual, platinum and stannous chloride have no effect on the determination of the base metals at these selected wavelengths, using the air-acetylene flame.

2.4 Ultraviolet - Visible Spectrophotometry of Cobalt

The absorption of ultraviolet or visible radiation, generally resulting from the excitation of bonding electrons in certain chemical species, has been widely used for quantitative and qualitative analysis. The ions and complexes of these elements that constitute the first two transition series of the periodic table, absorb visible radiation in one or more of their oxidation states. Their absorption bands are broad and strongly influenced by chemical environmental factors.

Divalent cobalt forms numerous complexes of various stereochemical types, of which the octahedral and tetrahedral ones are the most common. Of all the transition metal ions, cobalt forms the most tetrahedral complexes. With Co(II) being a d^7 ion, ligand field stabilization energies disfavour the tetrahedral configuration relative to the octahedral one to a smaller extent than any other d^n ($1 \leq n \leq 9$) configuration[32].

There are numerous cases in which octahedral and tetrahedral complexes of Co(II), having the same ligand exist in solution together in equilibrium. This is because of the small stability difference between the two stereochemical types.

In our study of Co(II) in ethanol/water solutions containing KSCN, we have two forms of the cobalt isothiocyanate complex $Co(NCS)_4^{2-}$. $Co(NCS)_4^{2-}$ in only water exists as the pink octahedral $Co(NCS)_4(H_2O)_2^{2-}$ complex shown in Figure 2.3 (b). If ethanol or acetone is added to the aqueous phase, the activity of the water is reduced and the complex transforms to a blue, tetrahedral configuration. See Figure 2.3 (a).

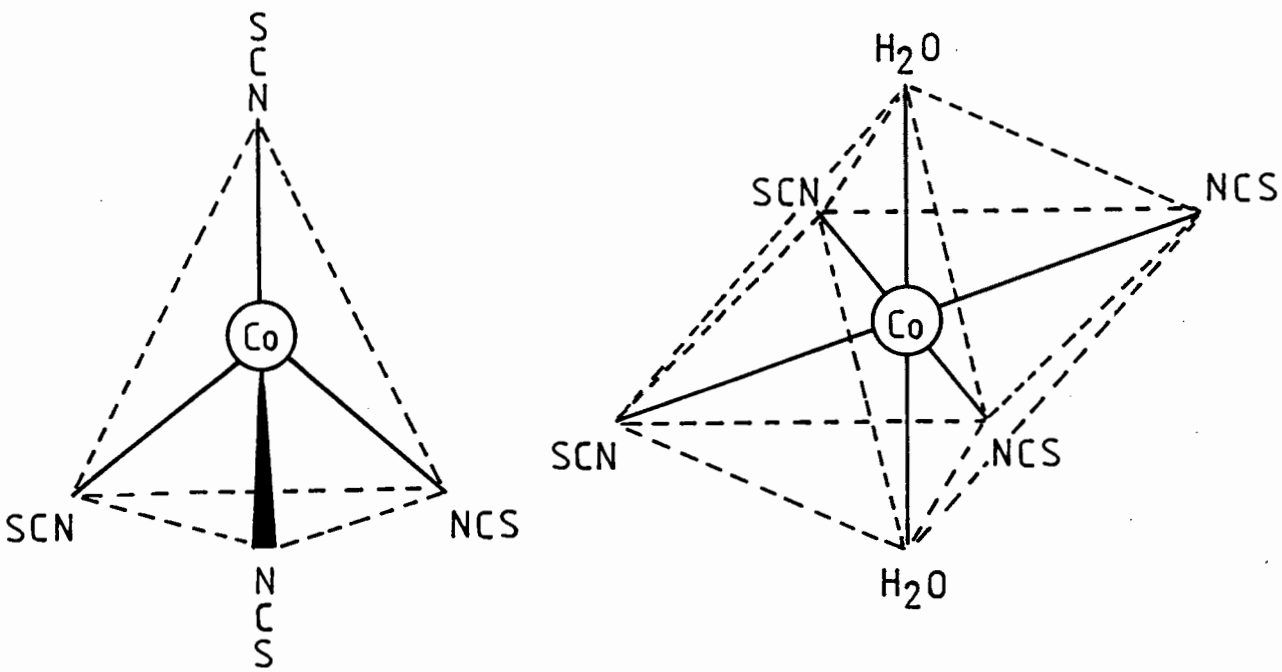


Figure 2.3 Two alternative structures for $Co(NCS)_4^{2-}$ in ethanol/water solutions containing Co(II) and KSCN.

An equilibrium exists between the two forms of $Co(NCS)_4^{2-}$ as shown below

$$Co(NCS)_4(H_2O)_2^{2-} \rightleftharpoons Co(NCS)_4^{2-} + 2H_2O$$

Shifts in this equilibrium are determined by:

(a) $EtOH:H_2O$: A direct relationship exists between this ratio and the proportion of complexes that are tetrahedral,

(b) Temperature: The higher the temperature the more the above equilibrium shifts to the left and

(c) $[SCN^-]$: Increasing the concentration of the thiocyanate ligand in solution, up to a limiting value of 12%, results in a shift in the equilibrium to the right.

Figure 2.4 illustrates the effect of the $EtOH:H_2O$ ratio on the equilibrium between the octahedral and tetrahedral structures of $Co(NCS)_4^{2-}$.

The tetrahedral form of $Co(NCS)_4^{2-}$ has a high molar absorption co-efficient (ε), whereas for the octahedral counterpart the reverse is true. So in order to achieve greater sensitivity in the detection of cobalt as its isothiocyanate complex, Sandel[43] recommends that the cobalt be determined in solutions of 50% water and 50% acetone. Ethanol was used in our work in preference to acetone because the latter was not recommended for the plastic tubing we used.

Figure 2.5 shows typical calibration curves for $Co(NCS)_4^{2-}$ where λ_{max} = 618 nm was used. Calibration curves are linear for the cobalt concentration range 0-100 ppm if the $EtOH:H_2O$ ratio $\leq$ 1.

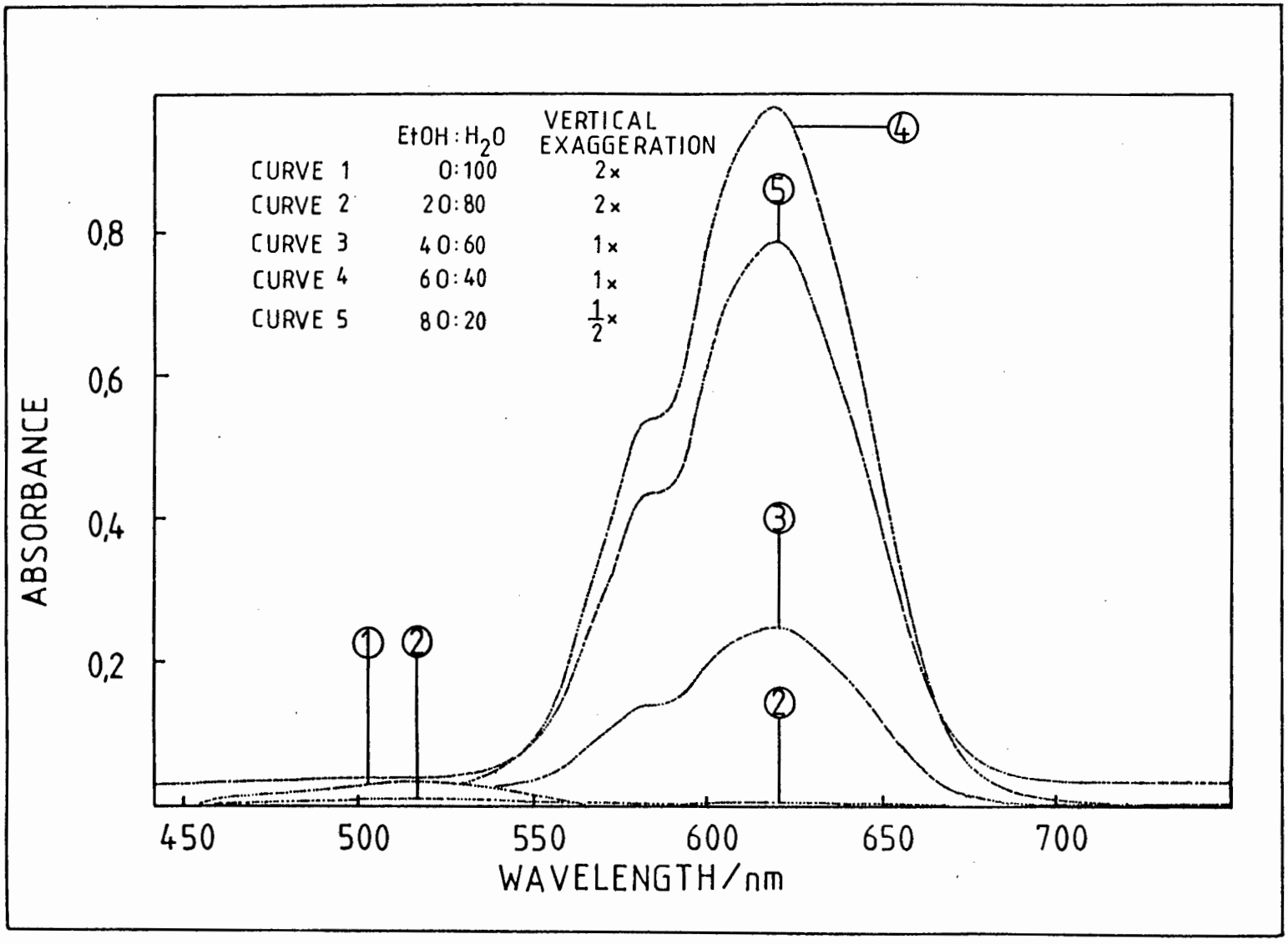


FIGURE 2.4 The Effect of the EtOH:H_2O ratio on the visible spectra of $Co(NCS)_4^{2-}$. All solutions contained 50 ppm Cobalt and were 0.4M with respect to KSCN.

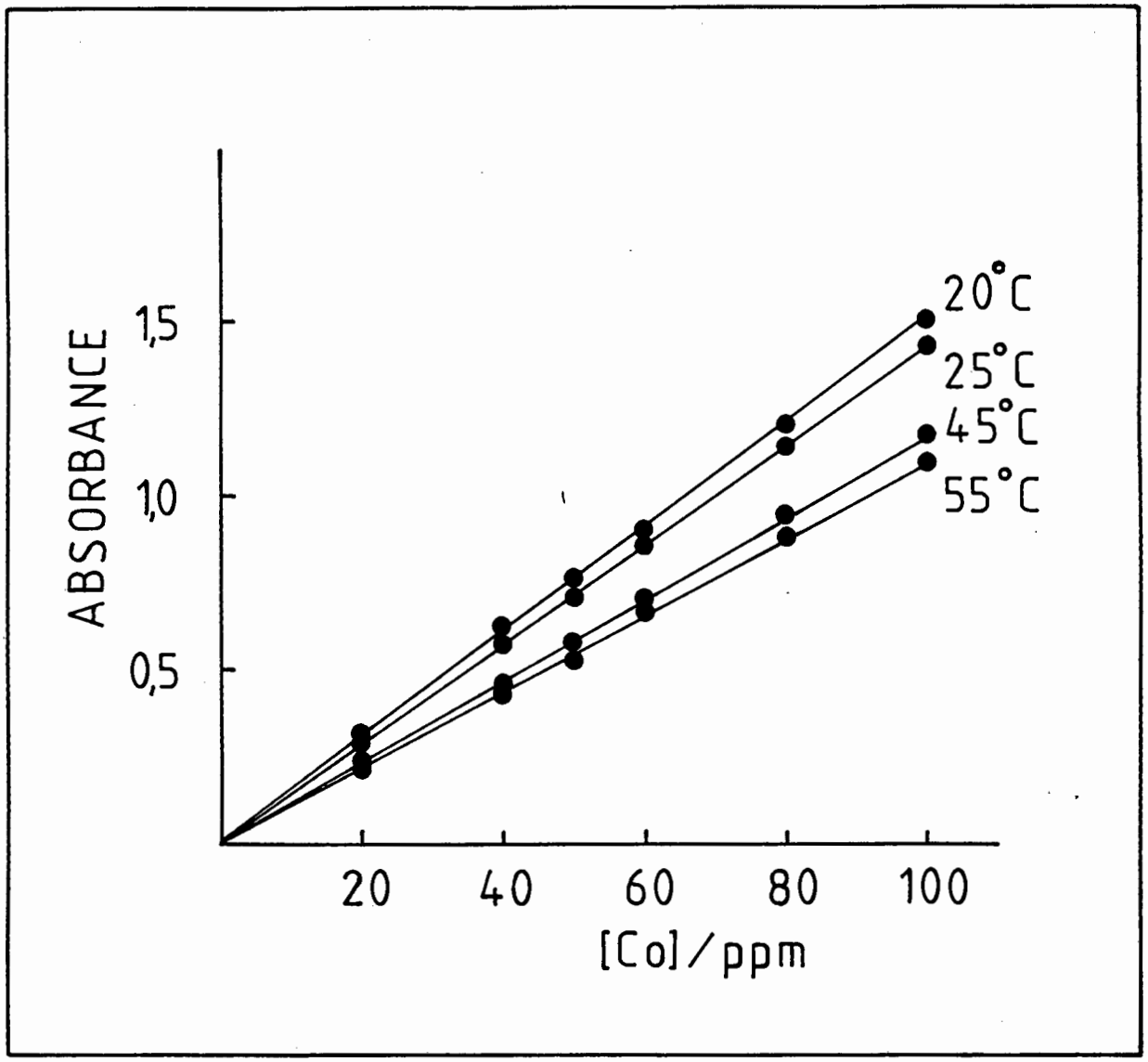


Figure 2.5 Calibration curves for cobalt in 0.5M KSCN, where the solution is 50:50 with respect to the EtOH:H_2O ratio

2.5 Ultraviolet - Visible Spectrophotometric Determination of Platinum

Since Wöhler discovered that tin(II) chloride reacted with platinum to give brightly coloured compounds[18], it has been used as a colorimetric reagent for platinum. Numerous authors have made detailed spectrophotometric studies of the platinum/stannous chloride/hydrochloric acid system, in an attempt to determine the stoichiometry of the platinum complexes in solution.

A period of 30 minutes is required to ensure that mixtures of platinum and tin solutions have reached a state of equilibrium, in which maximum colour intensity has been achieved. Spectra of the platinum-tin chloride complexes are affected by temperature, Sn:Pt ratio, hydrochloric acid and platinum concentration. Wavelength scans from 300-600 nm were recorded.

2.6 Titrimetric analysis of Tin(II) using Potassium Iodate

Although tin can be assayed successfully by atomic absorption, the method does not differentiate between tin(II) and tin(IV). Because it is important to determine the quantity of tin(II) in our stannous chloride solutions, we adopted the well-documented titrimetric method of analysing for tin(II) in hydrochloric acid, by oxidation with potassium iodate[40]. The oxidation is thought to proceed through the following steps:

$$30\ SnCl_2 + 10\ KIO_3 + 60\ HCL \rightarrow 30\ SnCl_4 + 10\ KI + 30\ H_2O$$

$$2\ KIO_3 + 10\ KI + 12\ HCL \rightarrow 12\ KCL + 6\ H_2O + 6\ I_2$$

$$3\ KIO_3 + 6\ I_2 + 18\ HCL \rightarrow 3\ KCL + 9\ H_2O + 15\ ICl$$

The overall reaction must thus be represented as:

$$2\ SnCl_2 + KIO_3 + 6\ HCl \rightarrow 2\ SnCl_4 + KCL + ICl + 3\ H_2O$$

The method involves the use of an immiscible organic solvent, such as chloroform or carbon tetrachloride, with the end-point of the reaction being marked by the disappearance of the last trace of violet colour from the organic phase. This colour is due to the iodine formed during the reaction as a by-product. Iodine chloride (ICl) is not extracted and imparts a yellowish colour to the aqueous phase.

Hydrochloric acid concentrations of about 5 M, recommended by Vogel[40], were used in the iodate oxidation of tin(II). All titrations were performed under pure, deoxygenated nitrogen because of the rapid ease with which tin(II) is oxidised to tin(IV) by oxygen in the air.

Table 2.4 lists some typical titration results obtained from freshly prepared stannous chloride solutions.

$SnCl_2 \cdot 6H_2O$ taken/mmoles	Sn(II) found mmoles	% Sn^{2+} of total Sn in $SnCl_2 \cdot 6H_2O$ soln.
0.600	0.580	97
1.200	1.179	98
1.800	1.766	98

Table 2.4 Results of tin(II) determinations by potassium iodate titration.

CHAPTER 3

CHAPTER 3

3.1 Preliminary Foam sorption study using $Co(NCS)_4^{2-}$

A number of considerations led to a preliminary investigation into the extraction of $Co(NCS)_4^{2-}$ by polyurethane foams, prior to the platinum study. At the outset, it was necessary to gain an understanding of the interaction between the foams and solutions and to identify any problems that may arise. With an appreciation for these problems, certain features were then incorporated into the design of the extraction apparatuses discussed in Chapter 7. This preliminary work required the use of substantial volumes of solutions containing an extractable species. Cobalt being cheaper than platinum was obviously a more suitable choice for this initial work.

To understand the mechanism or mechanisms by which chemical species extract into polyurethane foams, requires studying the rates at which these processes occur. Such a rate study entails monitoring the sorption process continuously and quantitatively. A stable, coloured chemical species that is readily extractable into the foam, provides an ideal subject to achieve this end. By using UV-VIS spectrophotometry in conjunction with a flow-through cuvette (Figure 7.3), a solution can be analysed from the instant the foam begins to absorb the coloured complex until the time the polyurethane reaches its maximum sorptive capacity.

The much studied $Co(NCS)_4^{2-}$/foam system[9,46,48] was chosen for the kinetics study, because it had the above-mentioned properties and can be determined with great sensitivity using absorptiometry.

3.1.1 The Effect of Temperature on the Distribution of Cobalt between solution and foam.

We list here details of a limited thermodynamic study of the $Co(NCS)_4^{2-}$/foam system. Our objective was to establish if K_d, the

distribution constant was proportional to a true equilibrium constant. K_d is defined here as,

$$K_d = \frac{C_i - C_e}{C_e}$$

where C_i is the initial concentration of the solution, prior to the addition of foam and C_e is the cobalt concentration of the solution at equilibrium with the foam. If K_d is proportional to a true equilibrium constant then the relationship,

$$\text{Ln}K_d \propto \frac{-\Delta G}{RT}$$

should hold and a plot of $\text{Ln}K_d$ against $^1/T$ should give a straight line. ΔG is the free energy change of the sorption reaction, R is the gas constant and T is the temperature measured in degrees Kelvin.

To verify the above thermodynamic expression we proceeded as follows. Using the apparatus shown in Figure 7.4 we established a set of calibration curves for cobalt, in water/ethanol solutions containing 0.4M KSCN, at different temperatures (65° - 20°C). Known quantities of foam were added and allowed to reach their capacities, in solutions for which calibration curves had been previously determined. The distribution constant was calculated as follows,

$$K_d = \frac{(\text{Abs})_i - (\text{Abs})_e}{(\text{Abs})_e}$$

where $(\text{Abs})_i$ is the initial absorbance of a solution containing no foam at a particular temperature and $(\text{Abs})_e$ is the absorbance measured at the same temperature once the foam was in equilibrium with the surrounding cobalt solution.

Figure 3.1 illustrates that only curves A and B display a

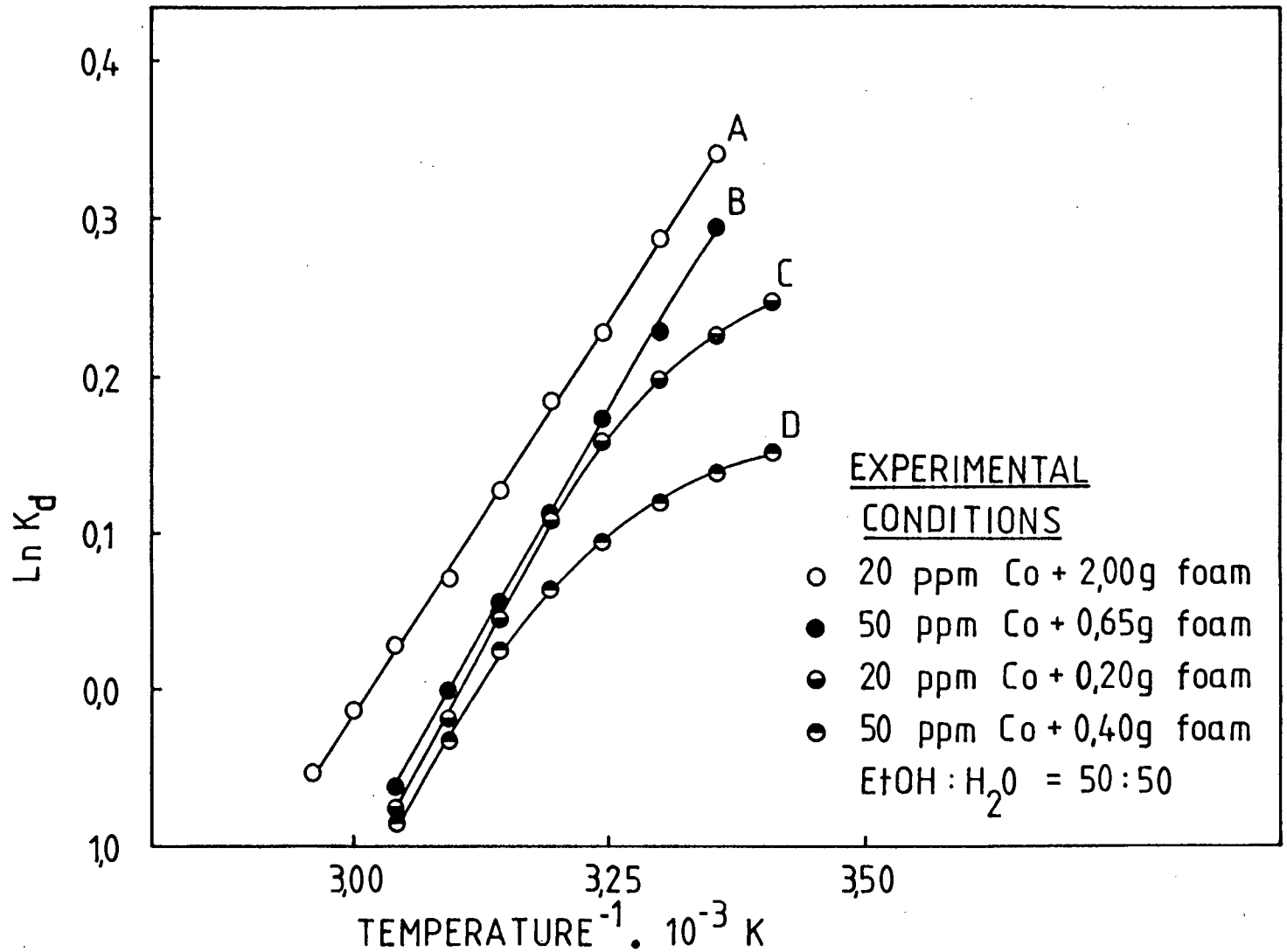


FIGURE 3.1 The plot of Ln K_d versus $^1/T$ for the $Co(NCS)_4^{2-}$/foam system

reasonable linear correlation between LnK_d and $^1/T$ for the temperature range studied (20° - $65^\circ C$). In the case of curves C and D, they are linear at the higher temperatures but deviate from this trend at temperatures lower than 45° and $40^\circ C$ respectively.

Linearity of the curves is apparently related to a foam mass : cobalt mass ratio. The higher this ratio the greater the tendency toward linearity. Hence it may be concluded that the foam near its maximum sorptive capacity results in significant deviation from linearity. (See discussion in Chapter 6).

3.1.2 The effect of temperature on the Sorbtive Capacity of the foam for Cobalt

Initial qualitative experiments carried out with the cobalt-foam system illustrated how, at room temperature the cobalt complex readily extracts into the polymer. In terms of the thermodynamic equation $LnK_d \propto \frac{-\Delta G}{RT}$, K_d is large and so the sorption process is accompanied by a large decrease in the free energy ΔG of the system. From this equation we can therefore infer that any increase in the solution temperature T, will result in lower K_d values i.e. less cobalt will sorb into the foam. This was confirmed in the previous section.

To determine foam capacity measurements for cobalt as a function of temperature we performed a number of experiments. At four different temperatures a series of solutions containing potassium thiocyanate and varying concentrations of cobalt were allowed to equilibrate with 100 mg quantities of foam.

Again the effect of temperature on the molar absorption coefficient (ε) of the solution has to be taken into account when determining the

amounts of cobalt sorbed into the foam. As before the mass of metal extracted into the polymer, is determined by the difference between the initial concentration of the solution at a particular temperature and the concentration of solution at the same temperature when it is in equilibrium with the foam.

From the results, isotherms can be plotted (Figure 3.2) that show that the capacity of the polyurethane, as expected, is indirectly related to the temperature. A significant feature of these graphs is that the differences in the capacities between 20° and $25^{\circ}C$ are much smaller than the differences between 45° and $55^{\circ}C$. This suggests that at a certain temperature below $20^{\circ}C$ the capacity of the foam will reach a maximum value.

3.1.3 The effect of the Initial Cobalt concentration of the solution upon the Capacity of the foam

Figure 3.2 also illustrates how, as the initial cobalt concentration of the solution increases so does the capacity of the foam for the metal. Above an initial solution concentration of 80 ppm cobalt, however, the capacity of the foam at a particular temperature reaches a maximum.

It is obvious from the foregoing, that when quoting a foam's

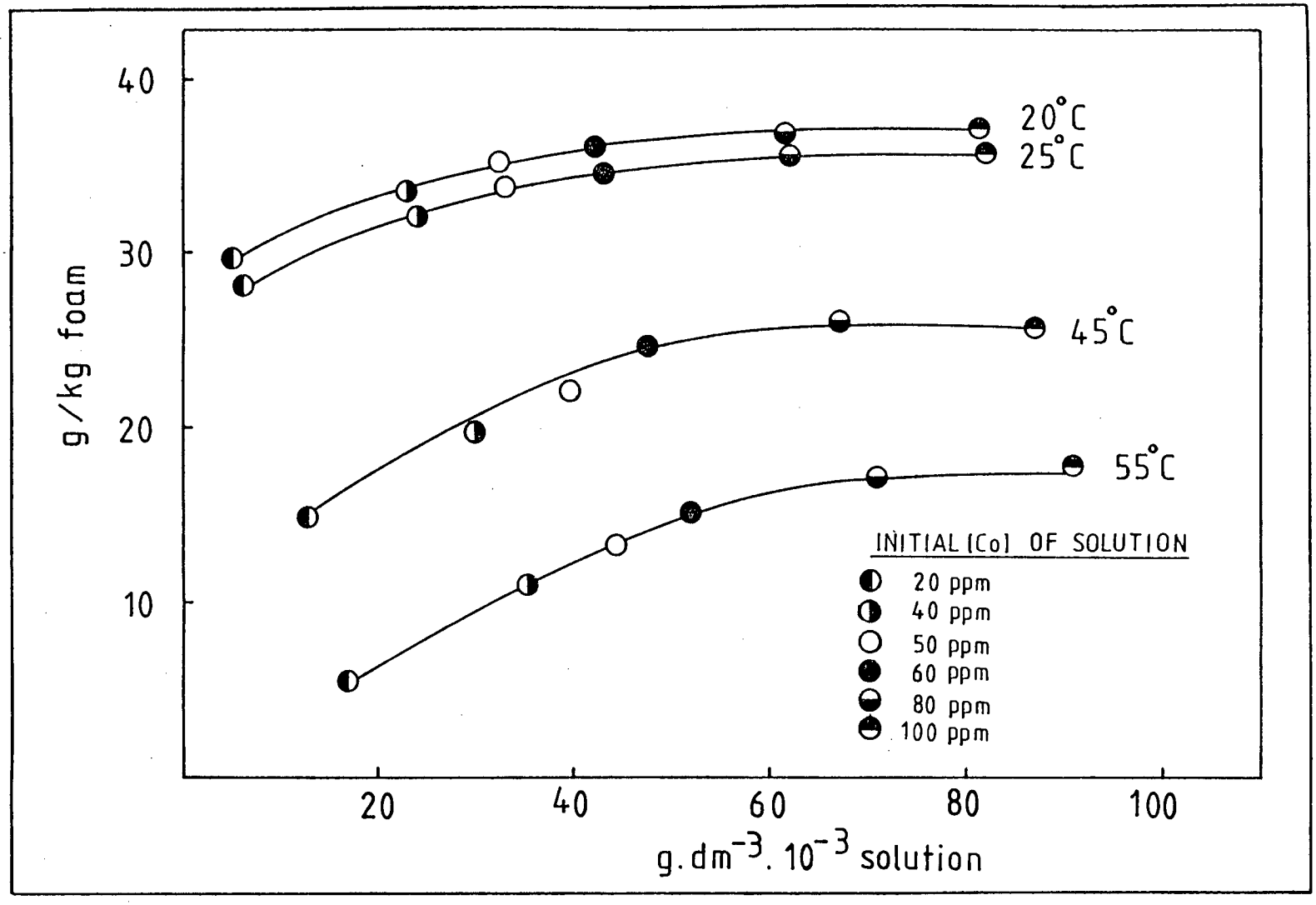


FIGURE 3.2 Isotherms shown here represent the amount of Cobalt on the foam versus the amount of Cobalt left in solution at equilibrium, for the $Co(NCS)_4^{2-}$/foam system. The amount of foam used = 100mg

capacity for a particular metal, one should state conditions of temperature and initial solution concentration. From Figure 3.2 we expect that at some temperature below 20°C and at some initial concentration of cobalt above 80 ppm, we will achieve a maximum capacity. The largest capacity we have achieved in this set of experiments was 0.61 moles/kg compared with 0.47 moles/kg achieved by Hamon *et al.*[9] and 0.19 moles/kg reported by Maloney *et al.*[46]. Neither author quoted temperature or initial cobalt concentration with their capacity measurements.

3.1.4 The Stoichiometry of the sorbed Cobalt complex

In trying to identify a mechanism to explain the sorption process, it is necessary to characterise the sorbed species in the foam. By using micro-analysis we were able to confirm, as many other authors have accepted[9,46,48], that cobalt extracts into the foam as $Co(NCS)_4^{2-}$.

The stoichiometric determination of the sorbed species involved the following series of experiments. Firstly, C, N and H percentages were obtained for clean unloaded foams. In the next step a number of foams were immersed in KSCN solutions and then washed in distilled water and vacuum dried. Their micro-analyses were compared with those for the unloaded foams (Table 3.1). KSCN is obviously not retained to any great extent by the foam as the comparison of C, N and H percentage values show.

The quantity of cobalt extracted into polyurethane foams from KSCN solutions was determined. According to the literature cobalt extracts as its $Co(NCS)_4^{2-}$ complex[9,46,48] and assuming this is true and knowing the capacity of the foam for the cobalt, we were able to predict C, N and H percentages.

For loaded foams Table 3.1 shows a good correlation between predicted and observed values.

	%C Determined/Predicted		%H Determined/Predicted		%N Determined/Predicted	
Unloaded foams	61.3		8.9		4.9	
Foam loaded with KSCN and washed	61.0		8.9		5.0	
Foam loaded with Cobalt then washed	54.5	55.5	7.6	7.7	6.3	6.7

Table 3.1 Micro-analysis of Loaded and Unloaded Polyurethane Foams

A simple test that involved placing a small block of foam into a pink solution of cobalt and KSCN containing no alcohol, showed that the initially white foam gradually turned blue, as the polyurethane evidently extracts the cobalt complex in its tetrahedral form.

3.1.5 The Rate of Sorption of Cobalt by Polyurethane Foam

For kinetic purposes it is convenient to classify a reaction as;

(a) Homogeneous, if it takes place in a single phase, i.e. in a solution or

(b) Heterogeneous if it proceeds at a phase boundary e.g. at the walls of a reaction vessel.

There is nothing fundamentally different between these two types of process. However, since reaction rates are measured in terms of concentration in the homogeneous medium and not at the phase boundary, the treatments of homogeneous and heterogeneous reaction rates are formally different.

The reaction, $2K^+ + Co(NCS)_4^{2-}$ aqueous $\rightleftharpoons$ $\overline{K_2Co(NCS)_4}$ foam, occurs

between two phases i.e. solution and foam and may be classified as a heterogeneous reaction, but because we measure the change in concentration of metal in solution (homogeneous medium), we assumed it valid as a first approximation to treat the extraction as a homogeneous process.

The law of mass action states that the rate of chemical change varies directly as the active concentrations of the reactants. For the homogeneous reaction,

$$A + B \rightleftharpoons \text{PRODUCTS}$$

in which the active concentrations of molecules A and B are equal to their actual concentrations in the reacting system, the rate is given by

$$-\frac{d[A]}{dt} = k[A][B] \text{ moles lit}^{-1} \text{ sec}^{-1}.$$

This mathematical formulation of the mass action law is known as the rate expression and k is the rate constant for a particular reaction. The rate constant k remains unchanged throughout the reaction and provides a more convenient measure of reaction velocity.

To obtain the characteristic rate constant k from our experimental data, it is necessary to know the number of concentration terms (reaction order) for the rate expression. In order to determine reaction order from our experimental absorbance-time curves (Figures 3.3 - 3.6) we used the integrated rate expressions shown below, for first and second-order behaviour. The order which gives constant k values is the correct overall order.

The integrated form of the rate expression for a first order reaction is

$$\text{Ln } \frac{[A]_o}{[A]_t} = kt \qquad \text{Equation 1}$$

where $[A]_o$ is the initial concentration of the reactant and $[A]_t$ is its concentration after time t. Since

$$[A]_o \propto Ae$$

and

$$[A]_t \propto At - Ae$$

where Ae and At are the absorbance readings at equilibrium and at time t respectively, then equation 1 rearranges to

$$\text{Ln} \frac{Ae}{At - Ae} = kt \qquad \text{Equation 2}$$

See Appendix 1 for derivation of Equation 2. If the sorption of the cobalt is a first-order reaction then a plot of $\text{Ln} \frac{Ae}{At - Ae}$ vs $^1/t$ will generate a straight line.

Data collected in the first 100 seconds of the sorption process is shown in Figure 3.3. Although the curves are non-linear, it should be noted that as we increase the foam to cobalt ratio, so the graphs lose much of their curvature and if we look at Figures 3.3(c) and 3.3(d) we see that in the first 20 and 60 second periods respectively, the curves are in fact approaching linearity. This suggests a pseudo first-order process in which the number of sites in the foam is effectively in excess and therefore constant.

Plotting our sorption data which was collected over 15 minute periods (Figure 3.4) we see the slopes of these graphs are not constant.

All other parameters remaining constant, the larger the mass of foam, the faster is the rate of cobalt sorption into the polyurethane. The foam must, therefore, be treated as a reactant. The integrated form of the rate expression for a second-order reaction is,

$$\frac{1}{[A]_o - [B]_o} \cdot \text{Ln} \frac{[A]_t [B]_o}{[A]_o [B]_t} \qquad \text{Equation 3}$$

where $[B]_o$ is the initial concentration of a second reactant and $[B]_t$ is its concentration at time t.

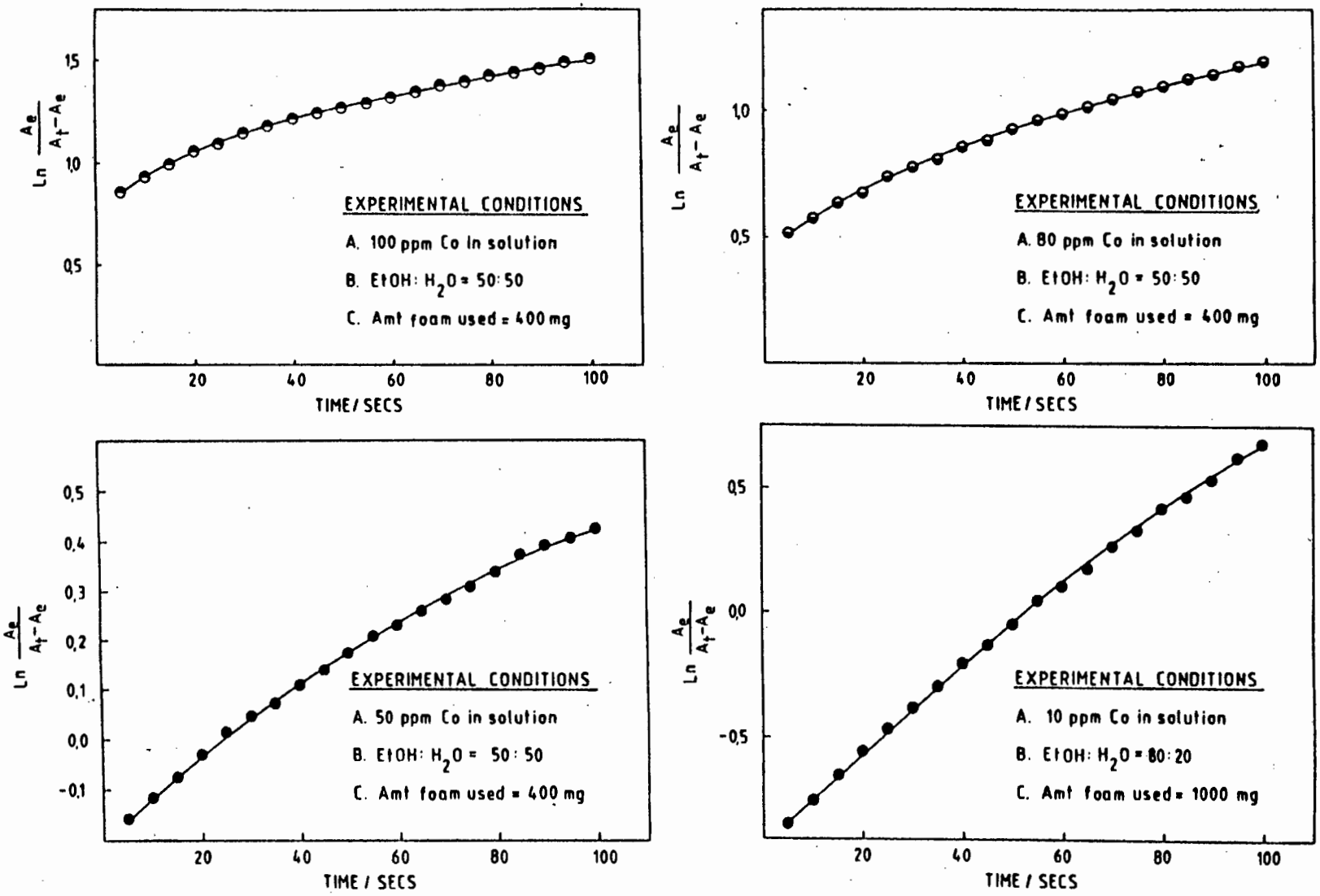


FIGURE 3.3 The rates at which Cobalt is extracted by polyurethane foams, are treated here with the integrated form of the rate expression for a first order reaction.

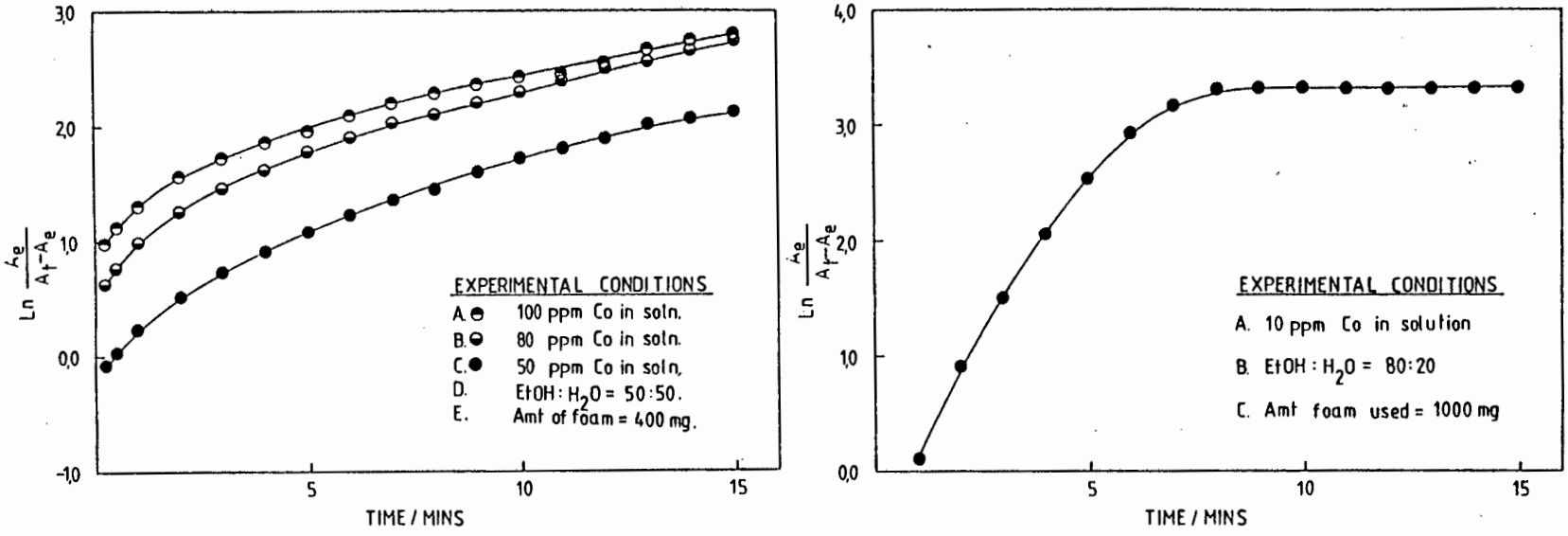


FIGURE 3.4 The rates at which Cobalt is extracted by polyurethane foams, are treated here with the integrated form of the rate expression for a first order reaction.

There are two difficulties in treating the foam as a term in the rate expression. Firstly, how can the number of 'sites' for a mass of foam be established and secondly, if the number of 'sites' are known how do we measure their concentration.

'Sites' are areas within the foam that are responsible for the extraction of certain species from solution. As mentioned previously, 'sites' may result from cations being engulfed in the polyether section of the foam, or they may result from the protonation of nitrogen atoms in the crosslinks of the polymer or protonated oxygen atoms in the polyether chain. Nitrogen and oxygen atoms within the foam having electron donor pairs could function as ligands to complex various species and thus behave as sorption 'sites'.

We have assumed, based on the cation chelation mechanism, that two 'sites' within the polyurethane extract one molecule of $Co(NCS)_4^{2-}$. If this is so then $[B]_o$ can be estimated by measuring at capacity, the total number of moles of cobalt isothiocyanate sorbed into the foam, for each kinetics experiment.

The second-order reaction curves shown here, Figures 3.5 and 3.6, were obtained from the same data used in generating the first-order reaction graphs. Again in Figure 3.5 we see an approach to a greater degree of linearity as we increase the foam to cobalt ratio. Comparing first and second-order reaction plots over a time intervals of a 100 seconds, we observe that the latter have larger linear portions. In Figure 3.6(a) we note that the curves are non-linear but in Figure 3.6(b) the initial 5 minutes of this plot is a straight line.

It is obvious from these graphs that the kinetics of sorption are not simple and are most probably neither first or second-order. It is

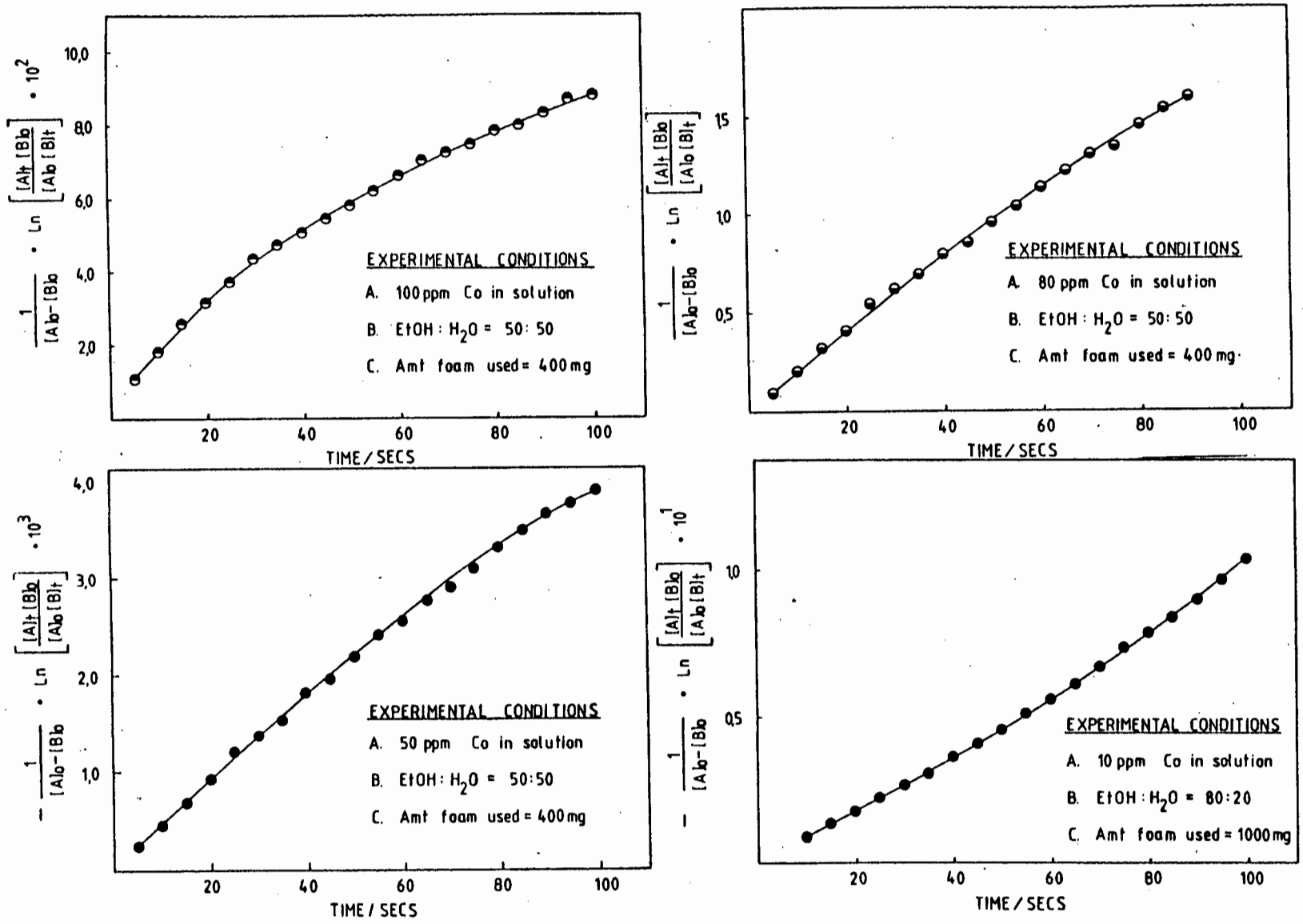


FIGURE 3.5 The rates at which Cobalt is extracted by polyurethane foams, are treated here with the integrated form of the rate expression for a second order reaction.

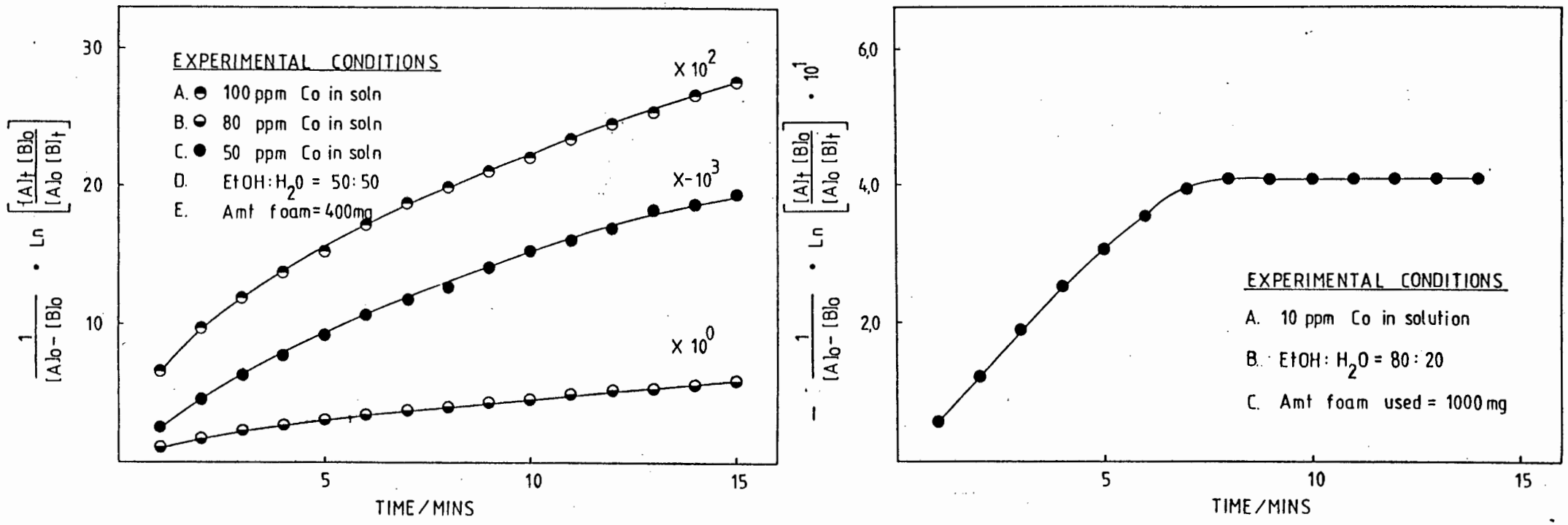


FIGURE 3.6 The rates at which Cobalt is extracted by polyurethane foams, are treated here with the integrated form of the rate expression for a second order reaction.

quite possible that if diffusion becomes the rate determining step it will complicate our simplistic approach to determining orders of reaction. Further work was shelved so that we could concentrate on the platinum sorption study.

3.2 Sorption of Tin by Polyurethane foams from HCl solutions containing no Platinum

In attempting to assign R_f values $\left(\frac{\text{moles Sn on foam}}{\text{moles Pt on foam}}\right)$ to platinum complexes extracted into the foam, it is essential at the outset, to know if any tin chloride not associated with platinum, will be accommodated within the foam. A known quantity of stannous chloride, which is typical of the amounts used in subsequent experiments, was dissolved in nitrogen purged solutions of varying HCl concentration. Identical masses of foam were allowed to equilibrate with these solutions. The results (Table 3.2) show that negligible amounts of tin extract into the solid organic phase at 1.0 and 2.0M HCl. At 3.0 and 4.0M HCl, however, an appreciable amount of tin is sorbed into the foam.

[HCl]/M	Mass Sn(mg) in initial solution	Mass Sn(mg) sorbed into foam
1.0	23.90	0.24
2.0	23.27	0.08
3.0	23.53	1.42
4.0	23.47	1.50

Table 3.1 Sorption of tin, not associated with platinum, into polyurethane foam.

3.3 Sorption of Platinum by Polyurethane foams from solutions containing no stannous chloride

Within experimental error negligible quantities of platinum were extracted from solutions of varying HCl concentration, in the absence of stannous chloride. Refer to Table 3.3.

[HCl]/M	Mass Pt (mg) in initial solution	Mass Pt (mg) sorbed into foam
1.0	10.15	0.05
2.0	10.13	0.06
3.0	10.09	0.09
4.0	10.05	0.04

Table 3.3 Sorption of platinum, not associated with tin, into polyurethane foam.

3.4 The Effect of the Hydrochloric acid concentration on the UV-VIS Spectra of the Platinum-tin compounds

Significant colour changes were observed in platinum-stannous chloride solutions, as the hydrochloric acid concentration was varied. Table 3.4 lists the observed colour changes for a particular platinum-tin(II) chloride solution.

Colour	[HCl]/M
Muddy brown	0.25
Reddish brown	0.50
Deep red	0.75
Deep red	1.00
Amber	2.00
Amber	3.00
Amber	4.00

Table 3.4 Colour changes in a solution containing 100 ppm Pt and where Ra = 4 as a result of varying [HCl]

In view of the above observations, we investigated the effect of hydrochloric acid on the visible absorption spectra of three different platinum-tin(II) chloride solutions. Spectra shown in Figures 3.7, 3.8 and 3.9 change dramatically as the acid concentration is raised from 1.0 - 2.0M. Traces for 2.0, 3.0 and 4.0M HCl, however, differ very little from each other.

It is obvious from the spectra that the nature of the platinum species is very similar in 2.0 - 4.0M hydrochloric acid, but very different from platinum compounds found in 1.0M acid conditions. In light of the work done by KuKushkin *et al.*[50], discussed in Chapter 6, it is not unreasonable to expect partial hydrolysis of the trichlorostannato platinum complexes in solution that have either low H^+ or Cl^- concentrations. It is therefore possible that a certain degree of hydrolysis occurs at 1.0M HCl but not at 2.0M or above. This would explain both the similarity of traces 2-4 and their difference from trace 1.

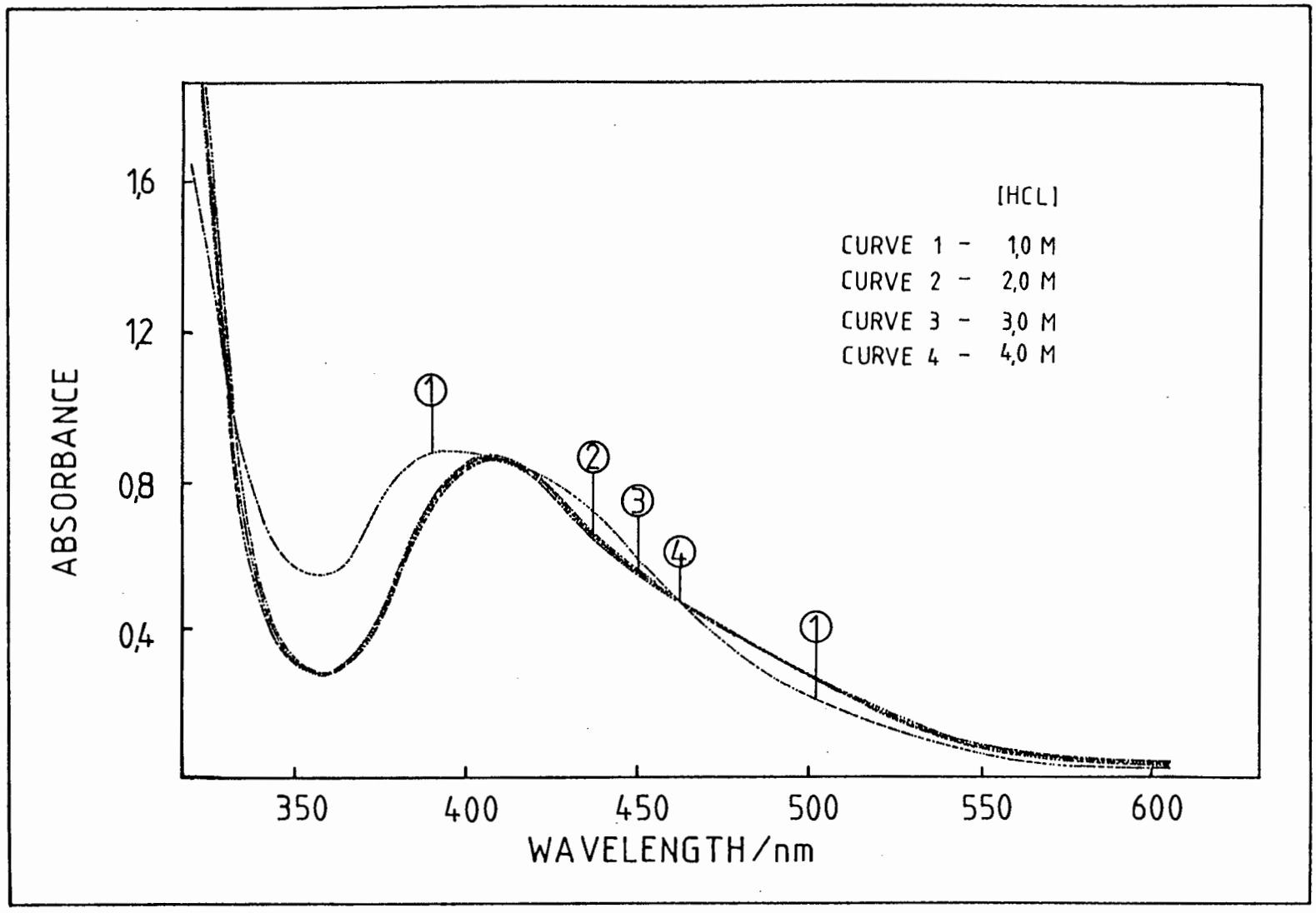


FIGURE 3.7 Visible absorption spectra for solutions containing a 100 ppm Platinum and a Sn(II):Pt(II) molar ratio of 10:1. The HCl concentration is varied.

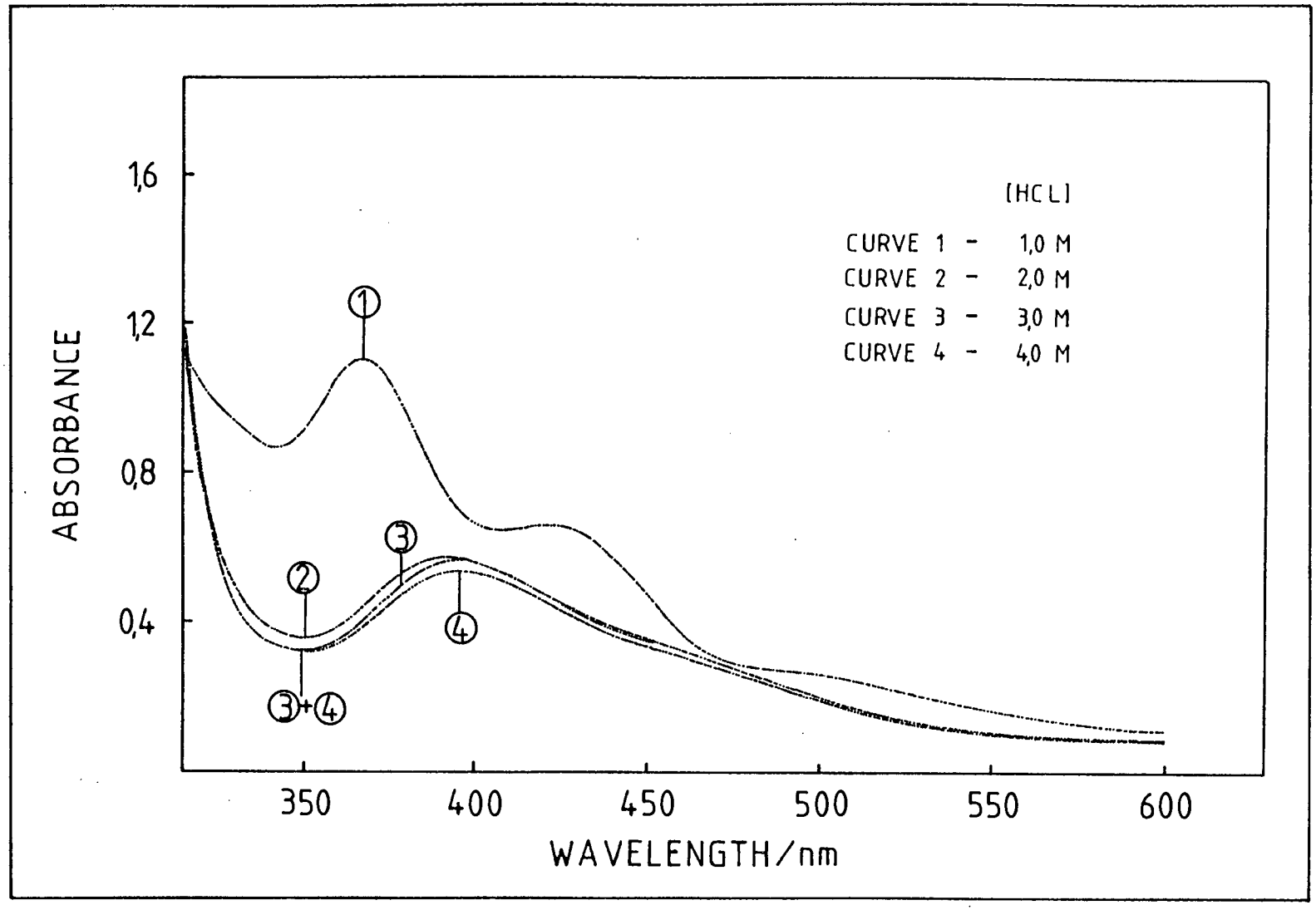


FIGURE 3.8 Visible absorption spectra for solutions containing a 100 ppm Platinum and a Sn(II):Pt(II) molar ratio of 5:1. The HCl concentration is varied.

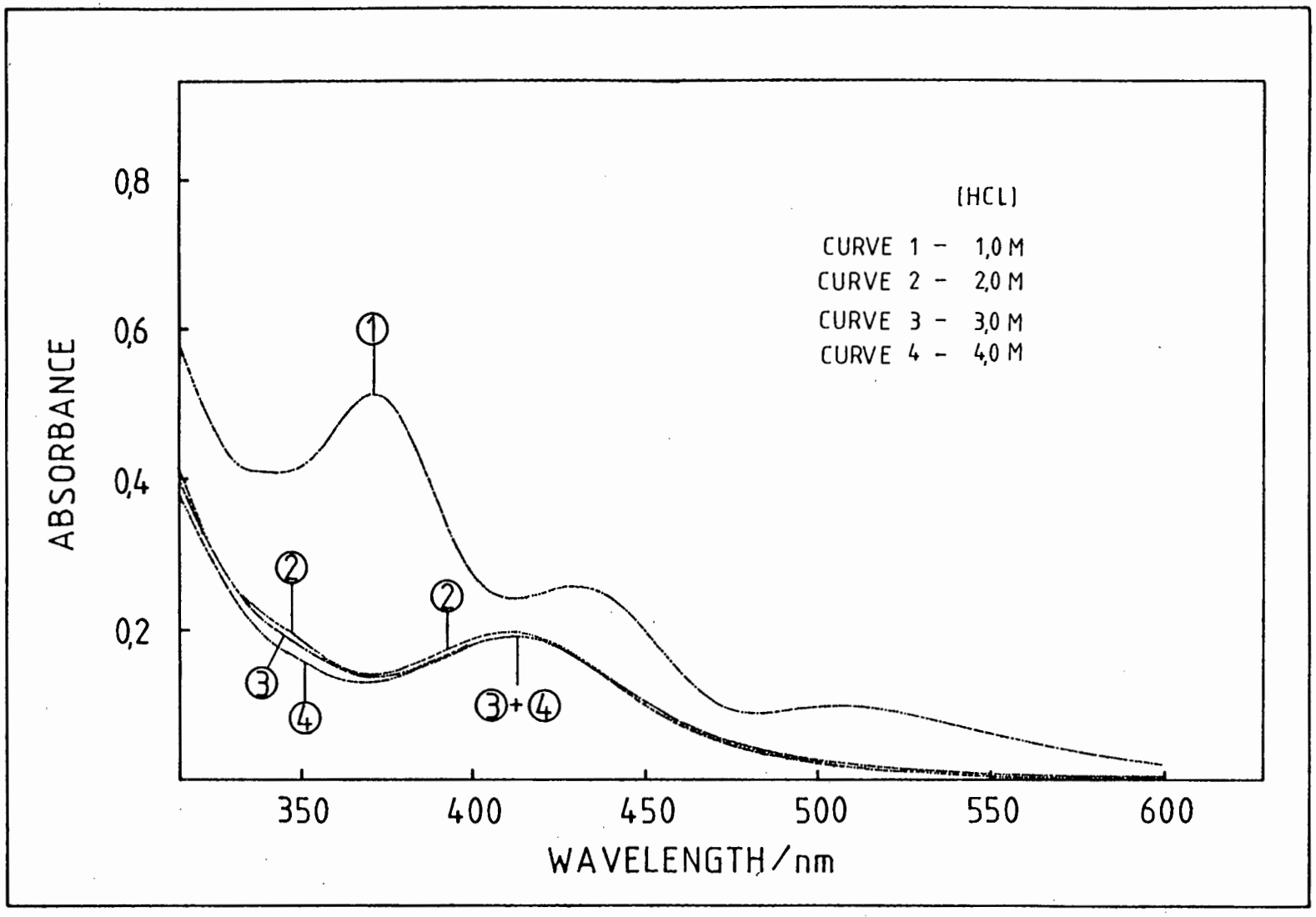


FIGURE 3.9 Visible absorption spectra for solutions containing a 100 ppm Rlatinum and a Sn(II):Pt(II) molar ratio of 2:1. The HCl concentration is varied.

The Sn:Pt molar ratio has a marked effect on the spectra of Figures 3.7, 3.8 and 3.9, which indicates the extent to which the character of the platinum complexes have changed. Table 3.5 lists the wavelengths of the various absorption maxima.

Sn:Pt	Absorption maxima/nm at 1.0M HCl	Absorption maxima/nm at 2.0-4.0M HCl
2:1	372 431 501	410
5:1	368 423	398
10:1	392	407

Table 3.5 Absorption maxima of solutions containing 100 ppm Pt and various quantities of stannous chloride

Limited work by other authors has been done on the effect of hydrochloric acid upon the distribution of platinum-tin(II) chloride complexes. Elizarova and Matvienko[25] have produced spectra for solutions that were 2.0M with respect to HCl and had Sn:Pt molar ratios of 2:1, 5:1 and 10:1. Their absorption maxima at 400nm is fairly similar to our maxima recorded at 410, 398 and 407nm.

CHAPTER 4

CHAPTER 4

4. The Sorption of Platinum by Polyurethane Foams

Prior to the addition of foam to solutions containing the platinum and stannous chloride, a period of 30 minutes recommended by Yates[39], was allowed to elapse to enable the platinum and tin(II) chloride to react until a steady state was reached. For the study of the rates at which platinum sorbed into the foam, the apparatus shown in Figure 7.5 was used. All other extraction experiments were performed on the equipment illustrated in Figure 7.6

The major objective of this study was to establish how certain parameters affected the efficiency of the foam in its extraction of platinum from hydrochloric acid solutions. Methods of analysis devised for the accurate determination of platinum and tin were considered satisfactory. Detailed experimental procedures are given in Chapter 7.

4.1 The Effect of Temperature

At room temperature the platinum-tin compounds displayed a marked tendency to extract into the foam much like the cobalt complex. We therefore expect as with the cobalt study, an inverse temperature-capacity relationship exists for the platinum-foam system.

Graphs in Figures 4.1 and 4.2 show that with one exception (Figure 4.2(c)), the capacity of the polymer to extract platinum increases as the temperature decreases. The exception to the general trend may represent a case of experimental error. A state of equilibrium appears to be reached between platinum complexes in the foam and those in solution within 3 hours.

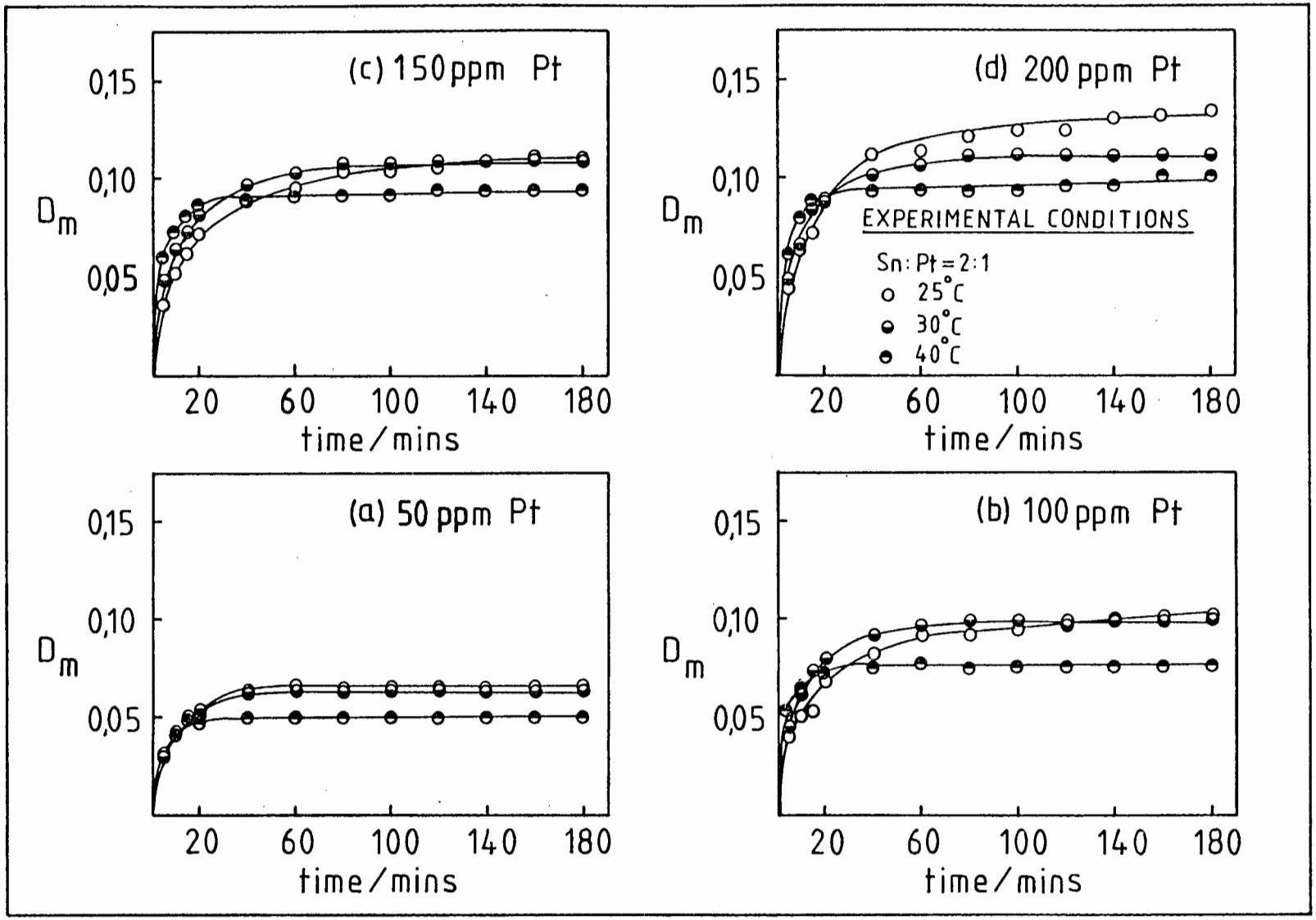


FIGURE 4.1 The Effect of Temperature upon the capacity of the foam and the rate at which it sorbs the noble metal.

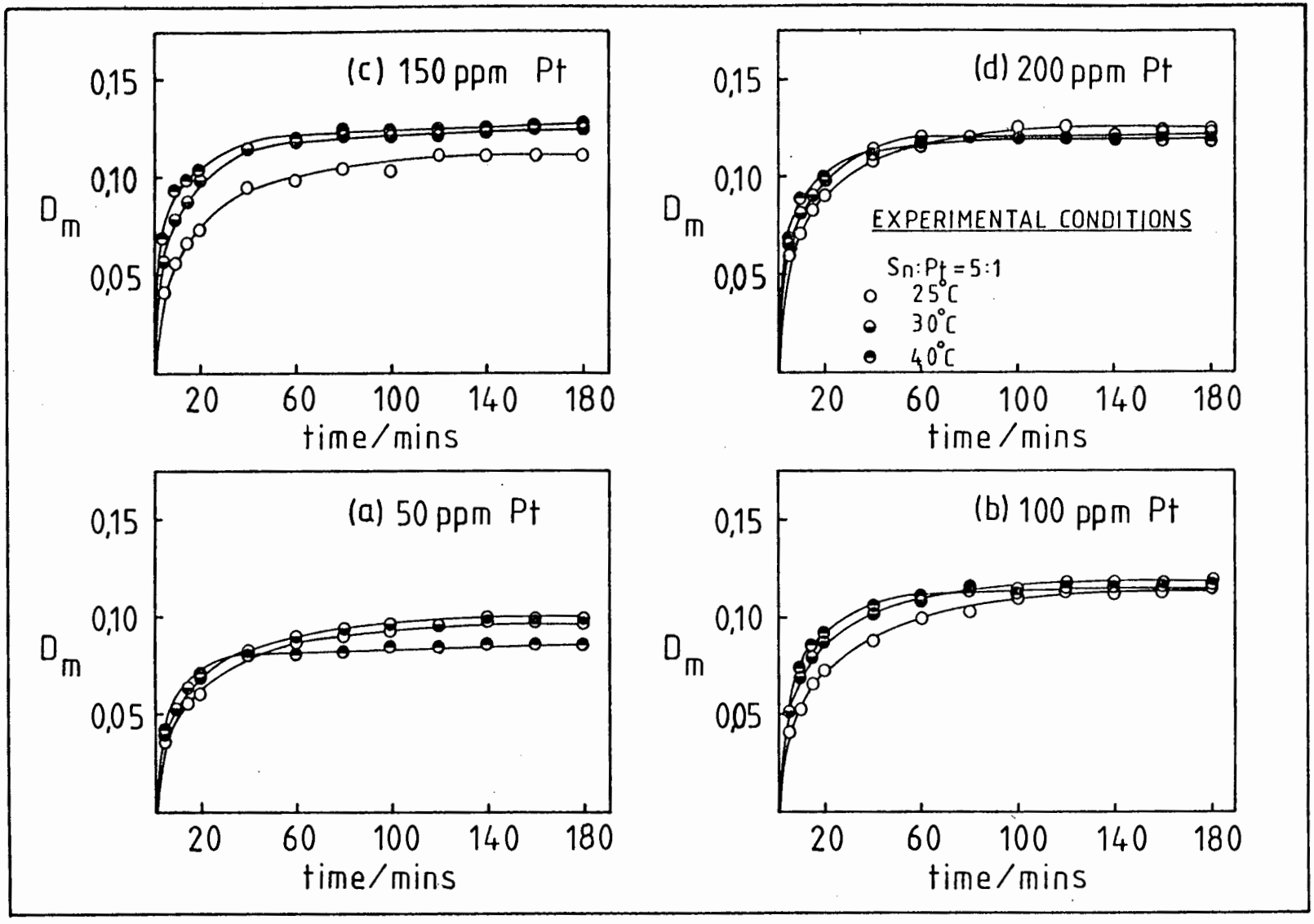


FIGURE 4.2 The Effect of Temperature upon the capacity of the foam and the rate at which it sorbs the noble metal.

Without exception in Figures 4.1 and 4.2, the rates of platinum sorption by the foam are shown to increase as we raise the temperature. This sorption rate-temperature dependence is explained in Chapter 6 by suggesting that a diffusion process operates between the solution and the foam.

Temperature, as well as determining the thermodynamics and kinetics of the extraction process, will also influence the equilibrium between different platinum-stannous chloride complexes. If certain of these complexes have a greater tendency to sorb than others, then temperature may well affect the capacity of the foam and the rate of extraction by virtue of its influence on the nature of the species in solution.

4.2 The Effect of the Initial Platinum Concentration

In our preliminary work we observed that up to a certain point, the higher the initial cobalt concentration of the solution the more of the metal was extracted into the polyurethane foam. We examine here if the same applies to the platinum-tin(II) chloride/HCl/foam system.

For all experiments, except one, shown in Figures 4.3 and 4.4, the capacity of the polymer to sorb the noble metal is directly related to the initial platinum concentration of the solution. In Figure 4.4(c) we note the anomalous capacity measurements, where the polyurethane has extracted less platinum from a 200 ppm platinum solution than from one that contains 150 ppm. Again this discrepancy may represent experimental error.

In considering the kinetic effects of the initial platinum concentration of the solution we observe in Figures 4.3 and 4.4 that for all cases, the greater the solution concentration of the precious metal the more rapid is the rate of sorption into the foam.

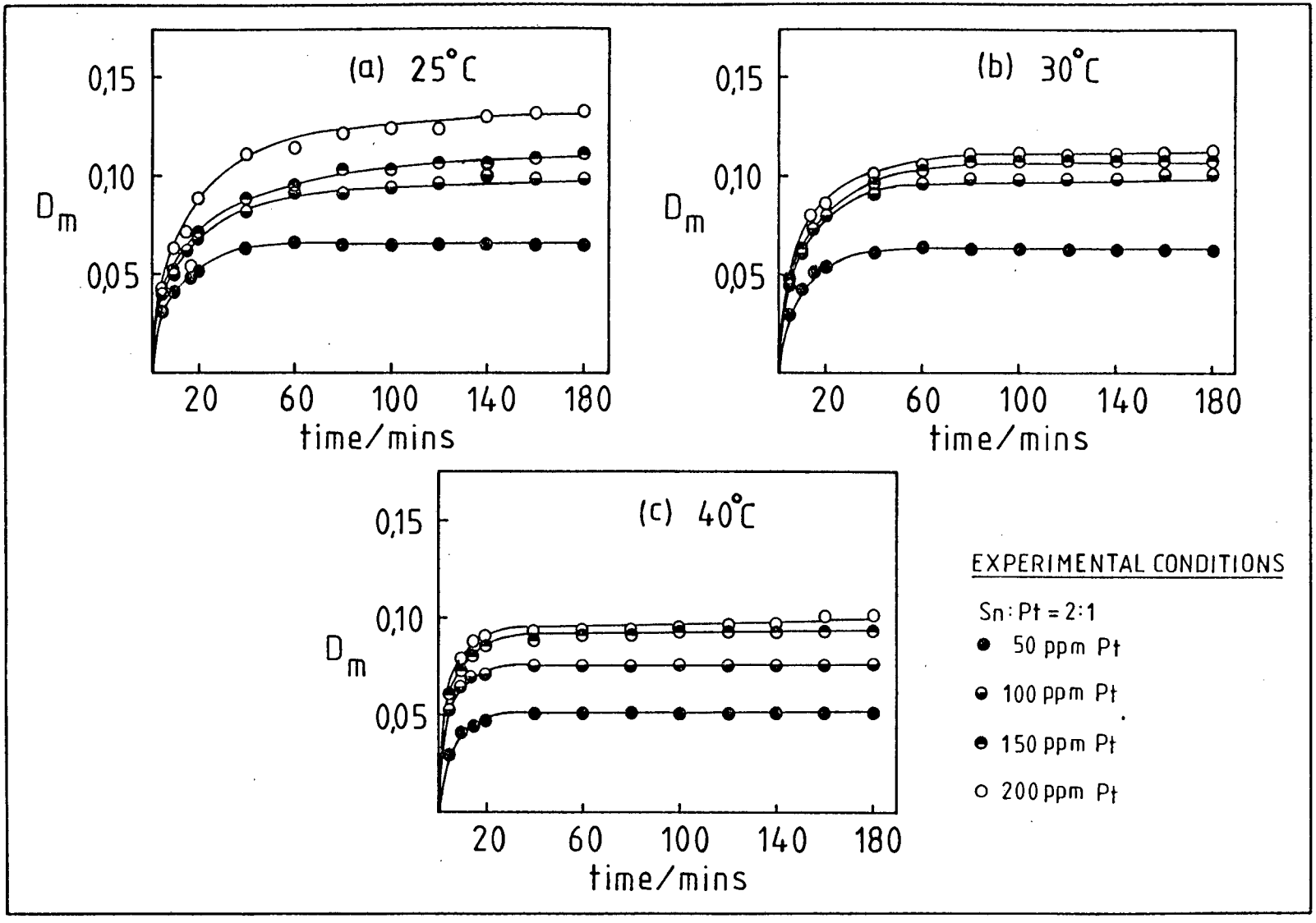


FIGURE 4.3 The Effect of the initial Platinum concentration upon the capacity of the foam and the rate at which it sorbs the noble metal.

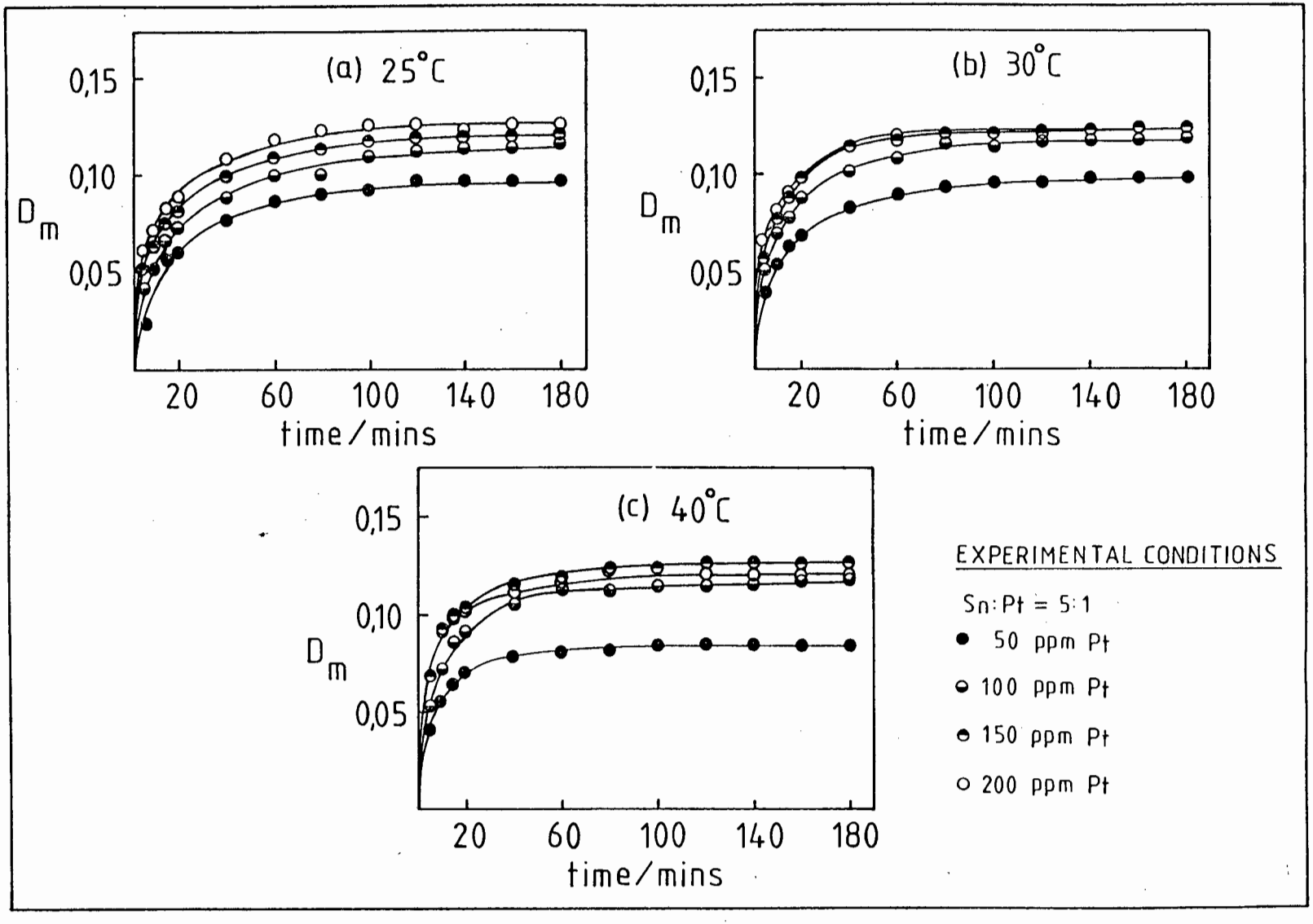


FIGURE 4.4 The Effect of the Initial Platinum concentration upon the capacity of the Foam on the rate at which it sorbs the noble metal.

The fact that in both the platinum and cobalt studies, the initial solution concentrations of these metals is directly related to the capacity of the foam and the rate of metal sorption, gives weight to the proposal that a diffusion process is operative at the liquid-foam interface.

4.3 The Effect of the Hydrochloric Acid Concentration

The hydrochloric acid concentration of the aqueous phase containing the platinum-stannous chloride complexes, is expected to have two major effects upon the foam's ability to sorb the precious metal. The hydrochloric acid concentration will affect the distribution of the platinum-tin species in solution and should also determine the extent to which 'sites' are formed in the foam.

Because the overall effect of varying the acid concentration on the foam/solution system was uncertain, we performed a set of experiments in which we were able to accurately determine the amounts of tin and platinum extracted into the foam, as we raised the hydrochloric acid concentration of the solution.

In Figure 4.5 we see that as we increase the hydrochloric acid concentration from 0.5 - 4.0M the quantity of tin extracted increases until a plateau is reached at approximately 2.0M. In the case for the sorption of platinum, a maximum is reached at 0.75M HCl after which the quantity of platinum extracted gradually decreases. At concentrations of HCl greater than 2.0M the sorptive capacity of the polyurethane for platinum remains essentially constant.

The almost identical spectra displayed in Figures 3.7 - 3.9 at $[HCl] \geq 2.0M$, represent a situation where the platinum-tin(II) chloride

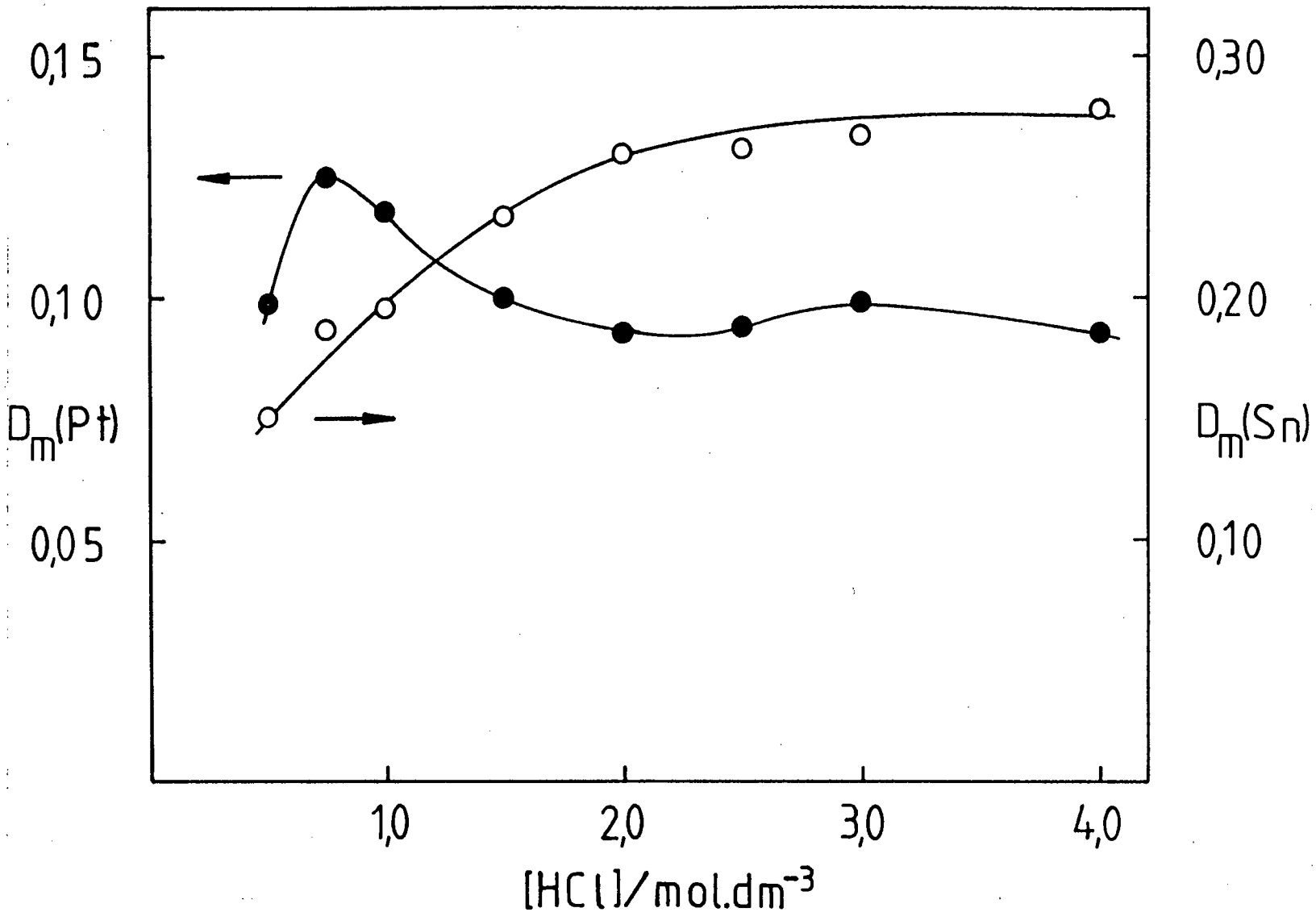


FIGURE 4.5 The Effect of [HCl] upon the foam's capacity to extract Platinum and Tin. Solutions used were kept at 25°C and had Sn:Pt molar ratios of 4:1 and contained 100 ppm Platinum. 50mg quantities of foam were used.

species remain relatively unchanged. This fact can be related to the constant extraction values for both platinum and tin over the same [HCl] range. It would appear that unless the distribution of the platinum-tin species in solution changes, the extraction values for platinum and tin will remain unchanged.

As the hydrochloric acid concentration of the solution was raised, we had expected the number of sorption sites to increase and hence result in an improved sorbtive capacity for the foam. The extraction trend for platinum has shown that this is not the case.

4.4 The Effect of Hydrogen Ion Concentration

The concentrations of both the hydrogen and chloride ions increase as we increase the HCl concentration. The observed effect of HCl concentration made us curious as to whether the H^+ or the Cl^- ions had the greatest influence on the extraction of platinum by the foam. A study in which the $[H^+]$ was varied was therefore undertaken.

Stannous chloride in chloride deficient acid media will undergo hydrolysis as shown in these equilibria;

$$SnCl_3^- + H_2O \rightleftharpoons SnCl_2(OH)^- + H^+$$
$$SnCl_2(OH)^- + H_2O \rightleftharpoons SnCl(OH)_2^- + H^+$$
$$SnCl(OH)_2^- + H_2O \rightleftharpoons Sn(OH)_3^- + H^+$$

To prevent this we use the acid mixture $HCl/HClO_4$ in solution. A fixed hydrochloric acid concentration of 0.75M maintains the $[Cl^-]$ at the required level to inhibit hydrolysis. By altering $[HClO_4]$ we vary the effective $[H^+]$.

Curves for the platinum and tin sorption versus the hydrogen ion concentration are shown in Figure 4.6. They are similar to those results

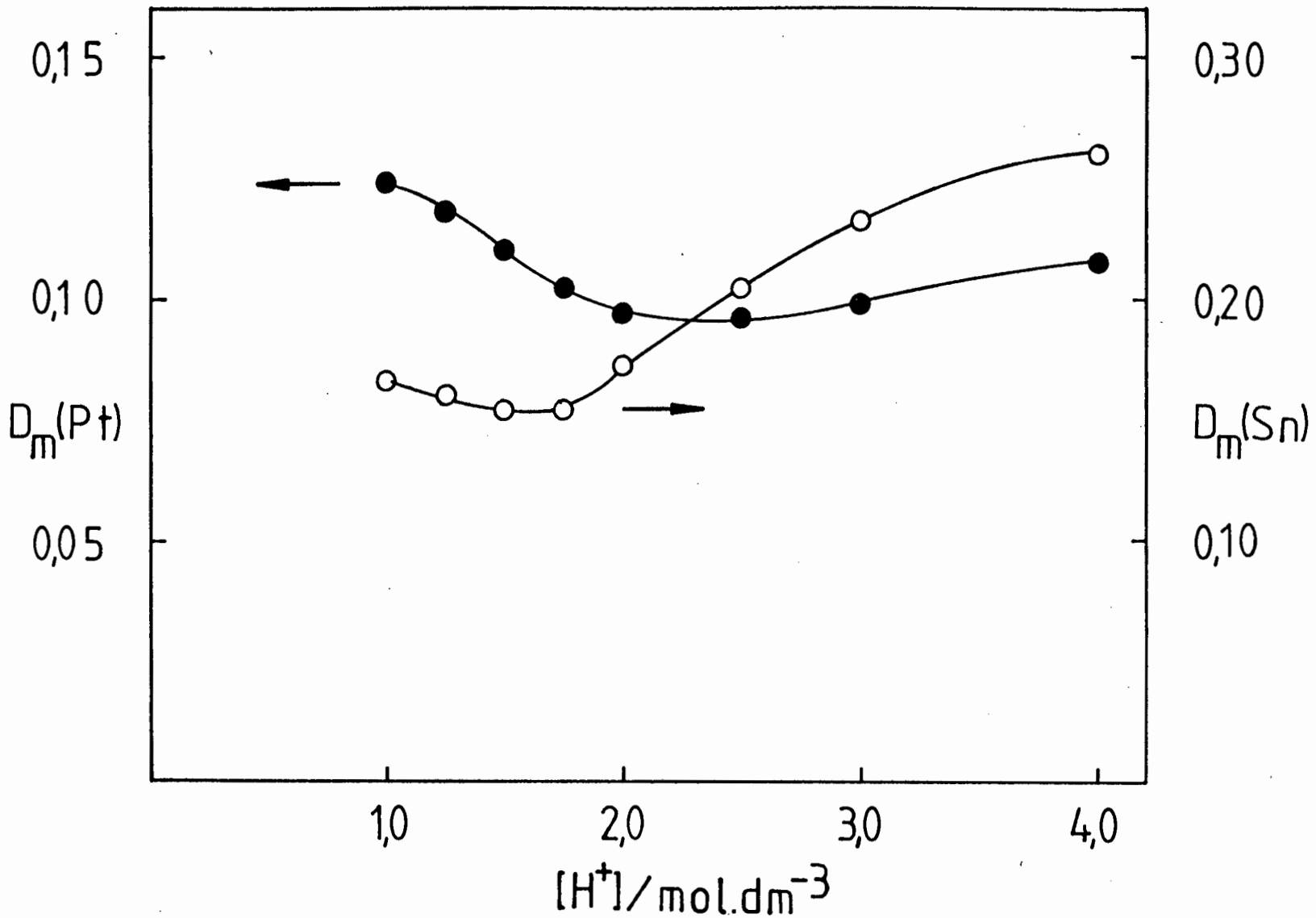


FIGURE 4.6 The Effect of $[H^+]$ upon the foam's capacity to extract Platinum and Tin. Solutions used were kept at 25°C and had Sn:Pt molar ratios of 4:1 and contained 100 ppm Platinum. 50mg quantities of foam were used.

in which the hydrochloric acid concentration was varied (Figure 4.5). The extraction of tin into the foam increases steadily as the $[H^+]$ increases from 2.0 - 4.0M. The maximum extraction for platinum occurs where the hydrogen ion concentration is equivalent to 1.0M, after which point the sorption of the metal decreases. From a hydrogen ion concentration of approximately 2.5M upwards the extraction of the noble metal increases slightly.

The similarity between Figures 4.5 and 4.6 suggests that the hydrogen ion rather than the chloride ion has the largest effect on the capacity of the foam to sorb platinum. If this is true, then differences in extraction values at various $[H^+]$ may be dependent on the extent to which platinum species in solution are hydrolysed. This possibility is discussed further in Chapter 6.

4.5 The Effect of Li^+, Na^+ and K^+ Cations

Hamon *et al.*[9], in support of the cation chelation mechanism, demonstrated that the degree to which $Co(NCS)_4^{2-}$, $Zn(NCS)_4^{2-}$, and the picrate anion were extracted, was determined by the type of cations present in solution. Hamon showed that the order of extraction followed the series $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+$. This order of cation preference is nearly identical to that of the 18-crown-6 derivatives[10,11].

By dissolving the chlorides of Li, Na and K into our precious metal solutions we were able to study their effects on the foam's ability to sorb platinum and tin. With the results we could then establish if the extractability of our platinum anions replicates the cation order series determined by Hamon.

For all solutions we chose an HCl concentration of 2.0M. This

decision was based on spectra shown in Figures 3.7, 3.8 and 3.9, in which we see that for hydrochloric acid concentrations of 2.0M and above the platinum-tin species in solution remain essentially unchanged. Therefore as we increase the chloride content of the solutions by adding the alkali metal chlorides, we will not expect to alter the distribution of the platinum-tin species

Referring to Figure 4.7, we note that all three cations adversely effect the foam's ability to extract the platinum from solution. The extent of this effect is related to the order $K^+ > Na^+ > Li^+$. In Figure 4.7(a) we see that by increasing the lithium chloride concentration from 0.75M to 1.50M we cause a steady but slight decrease in the foam's capacity for platinum.

The decrease in the mass distribution ratio seen in Figure 4.7(b) is more marked as we vary sodium chloride over the same concentration range. The change in platinum extraction is greatest between the values 0.50 and 1.00M NaCl.

In the case of potassium chloride we observe that the K^+ cation has by far the largest effect on the polyurethane's capacity and as in Figure 4.7(b) there is a definite step in the graph for the interval 0.50 - 1.00M KCl.

By determining the amount of tin that has been sorbed by the foam, presumably in association with platinum, we were able to obtain the average Sn:Pt molar ratio of the extracted species. Two notable features are evident in Figures 4.8(a), (b) and (c). Firstly R_f values are essentially constant as the cation concentrations are varied. Secondly, in comparing the average R_f values for each cation experiment, we see that they are very

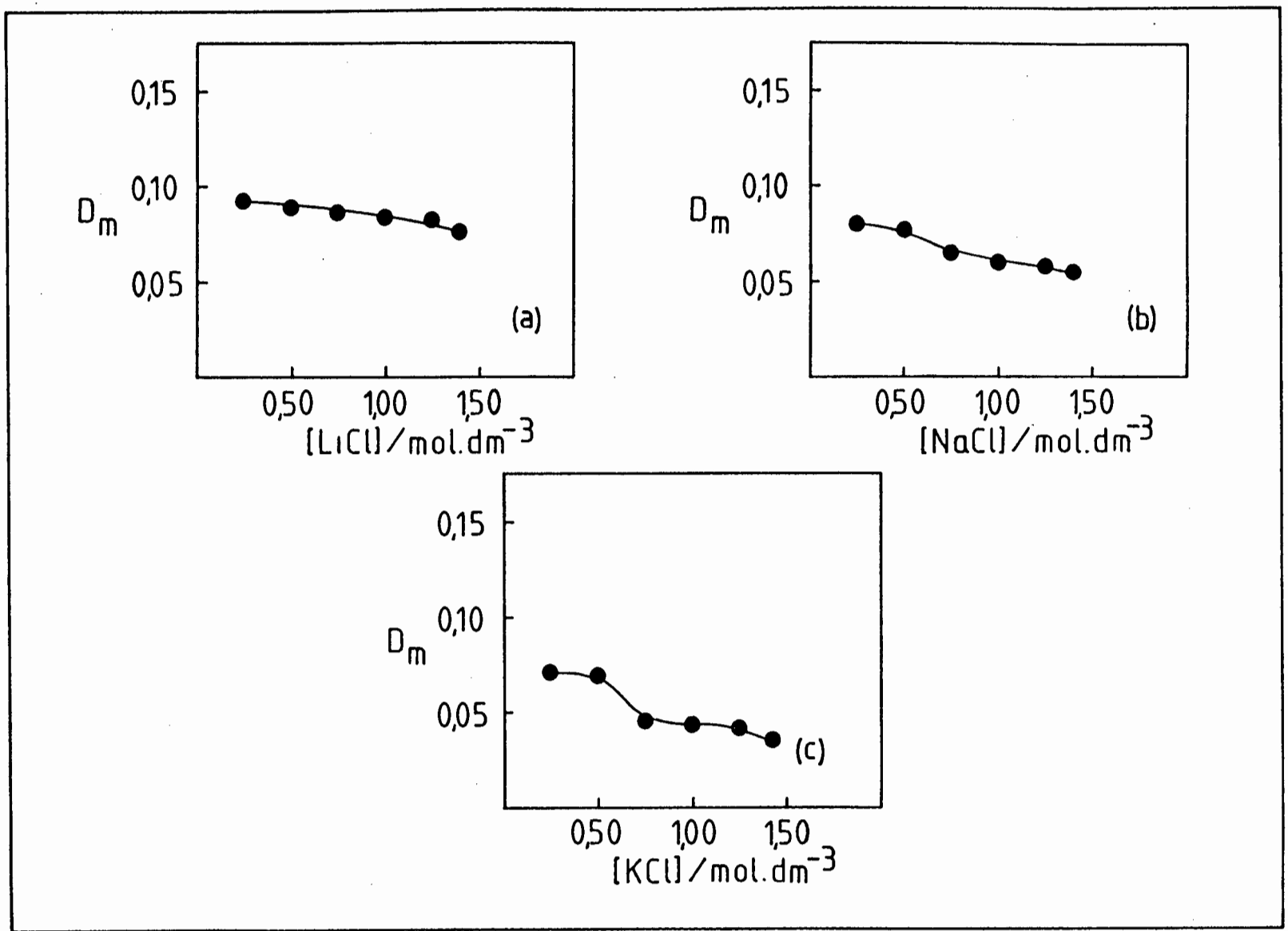


FIGURE 4.7 The Effect of the alkali metal cations, Li^+, Na^+ and K^+ on the foam's capacity to extract Platinum

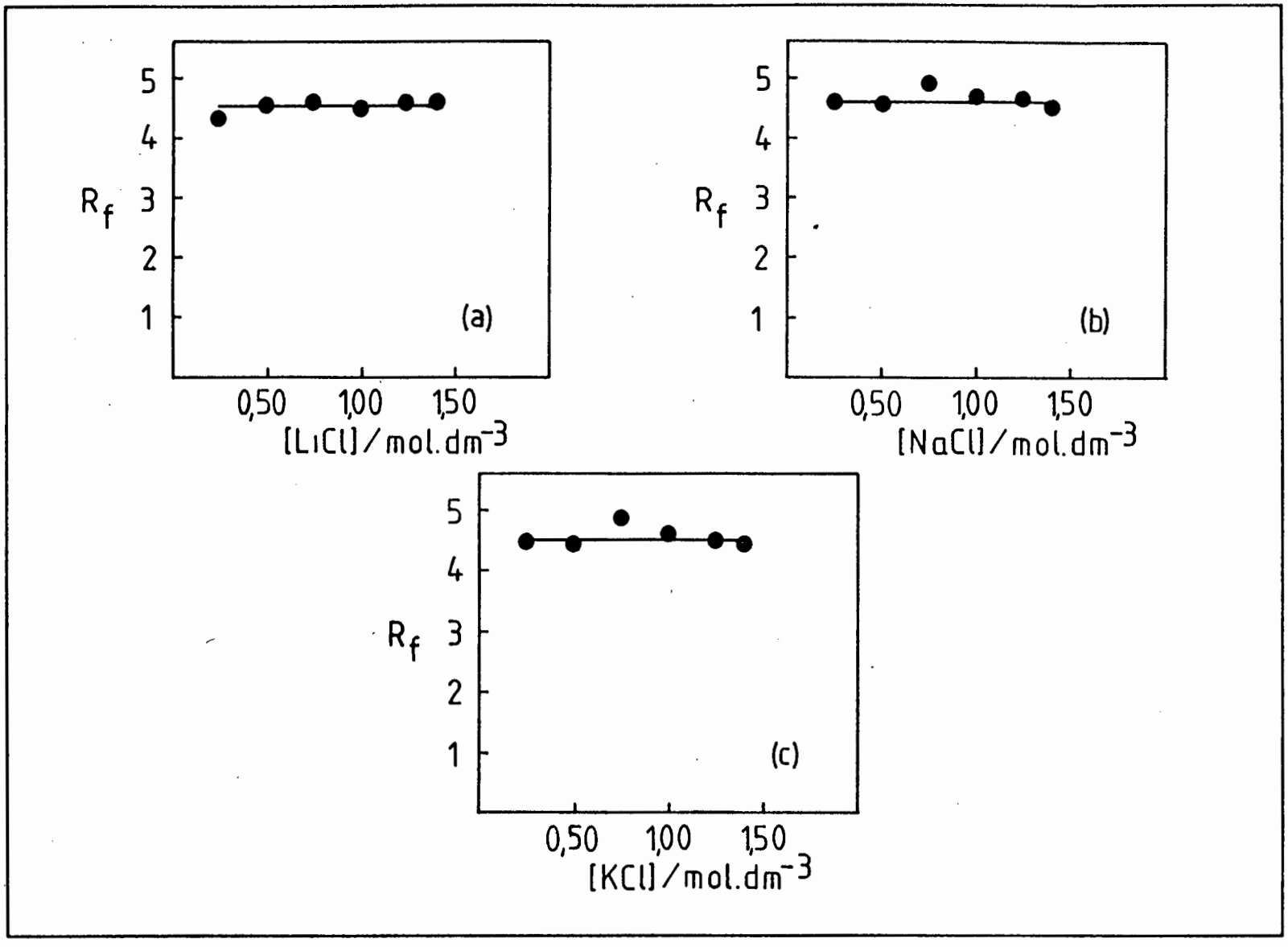


FIGURE 4.8 The Effect of the alkali metal cations, Li^+, Na^+ and K^+ on R_f

similar. The average R_f values for Na^+, K^+ and Li^+ experiments are respectively as follows, 4.67, 4.57 and 4.54. On the assumption that the platinum-tin species in the foam reflect the nature of the platinum complexes in solution, we suggest that the species in the aqueous phase are negligibly affected by the presence of the alkali metal cations.

4.6 The Effect of the Sn:Pt ratio (R_a) in the Initial Solution

The Sn:Pt molar ratio is known to affect the stoichiometry of the complexes in solution[27]. We may therefore expect changes in the rates of sorption and the capacity of the foam for the noble metal to occur, as a result of altering this ratio.

Considering each graph in Figures 4.9 and 4.10, we observe that in nearly all cases where $R_a = 5$, that the rates of sorption and the capacity of the foam for platinum, are greater than for conditions where $R_a = 2$. The exception to this trend is observed when foam is immersed in a 200 ppm platinum solution at 25°C. Looking at Figure 4.9(b) we see that the polymer's capacity for the precious metal and the rate at which it sorbs into the solid organic phase is larger at $R_a = 2$. This anomalous result may represent experimental error.

At $R_a = 5$, the $[Pt(SnCl_3)_5]^{3-}$ complex is believed to predominate in hydrochloric acid solutions. This fact and the observation that at $R_a = 5$, the rates of sorption and the capacity of the foam are larger than at $R_a = 2$, led us to the conclusion that the quinqueco-ordinate platinum complex may have a greater tendency to extract into the foam, than the square planar $[Pt(SnCl_3)_nCl_{4-n}]^{2-}$ (n = 1-4) and other platinum species.

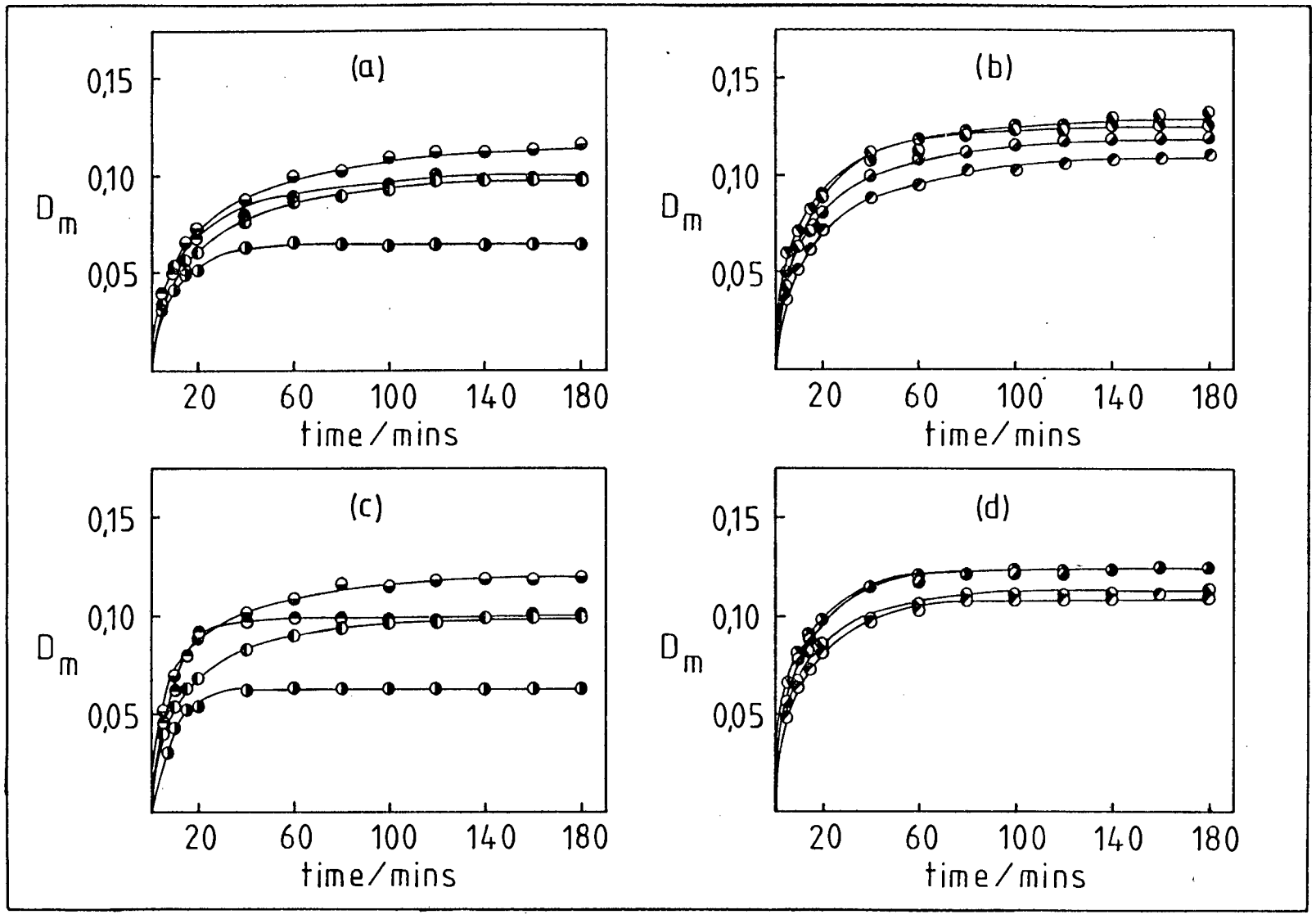


FIGURE 4.9 The Effect of R_a upon the capacity of the foam and the rate at which it sorbs the noble metal.

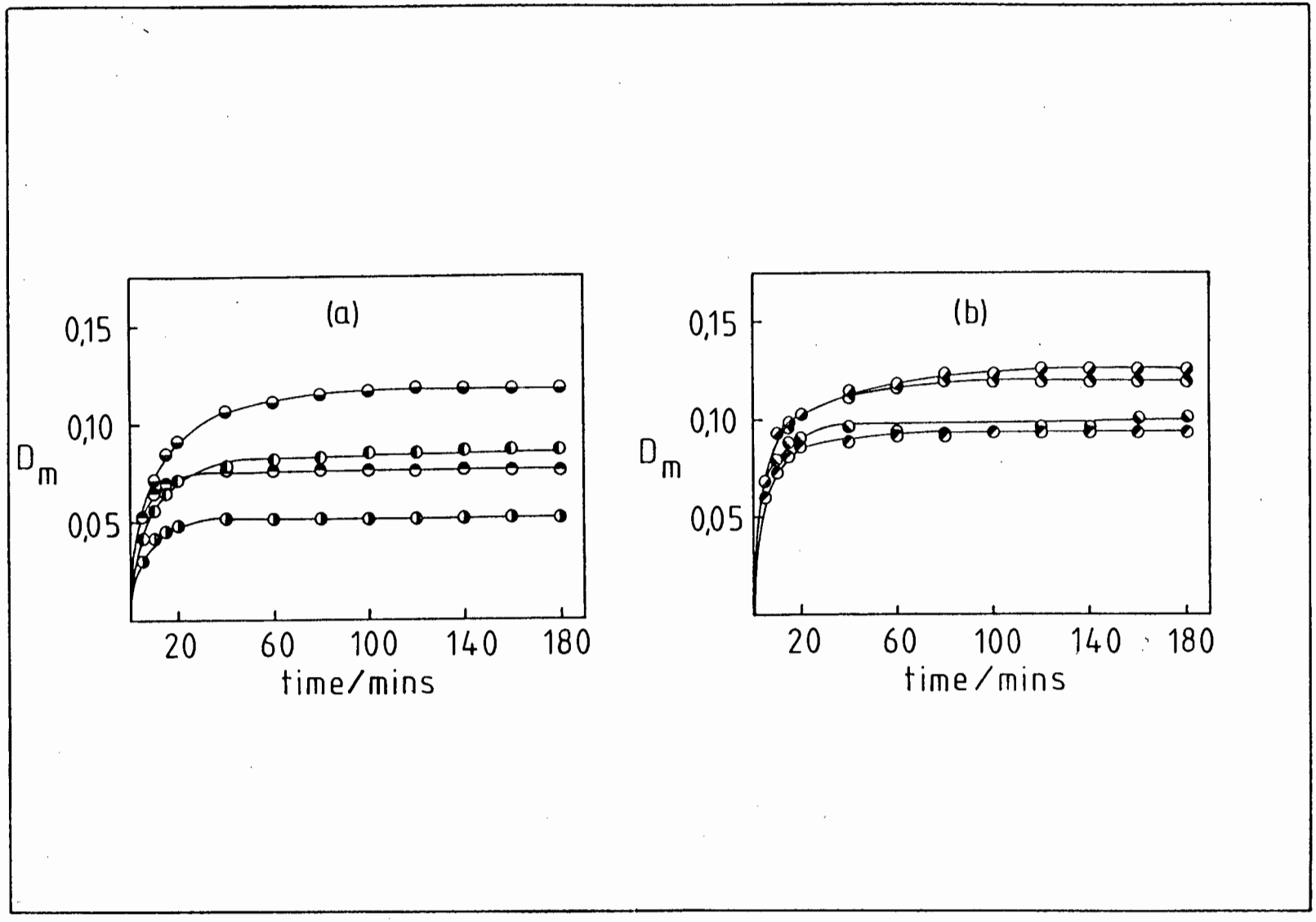


FIGURE 4.10 The Effect of R_a upon the capacity of the foam and the rate at which it sorbs the noble metal.

4.7 The Effect of varying R_a upon R_f and the Sorbtive Capacity of the Foam for Platinum

R_a has been shown to markedly affect the platinum complexes in solution, thereby influencing the rate and degree to which they are extracted by the foam. Stannous chloride being a relatively expensive input for the foam extraction system, it was decided to determine optimum R_a values for maximum platinum sorption. Different masses of foam were experimented with to see if maximum platinum extraction was achieved at the same R_a value.

Four series of experiments were conducted. Each series used a different mass of foam and within each series R_a values were varied between 2 and 40. All other conditions such as temperature, HCl and initial platinum concentrations were kept constant.

In Figure 4.11 we observe distinctly different platinum extraction graphs where different masses of foam have been used. It is apparent in the general levelling out of the trends in Figure 4.11, that the larger the mass of foam, the less critical the R_a value becomes in determining the maximum platinum extracted.

A major feature of Figure 4.11 is that maximum platinum extraction occurs at $R_a \approx 4$, irrespective of the quantity of foam used. Minimum extraction is observed at $R_a = 2$ where the masses of foam used were 75, 100 and 125mg. Where experiments were conducted with 50mg of polyurethane a minimum sorption value corresponded to $R_a \geq 10$.

In attempting to explain the different extraction trends in Figure 4.11, we considered the effect of R_a upon R_f. Assaying for tin and platinum in the hydrochloric acid solutions that were in equilibrium with the polyurethane foam, we were able to determine R_f.

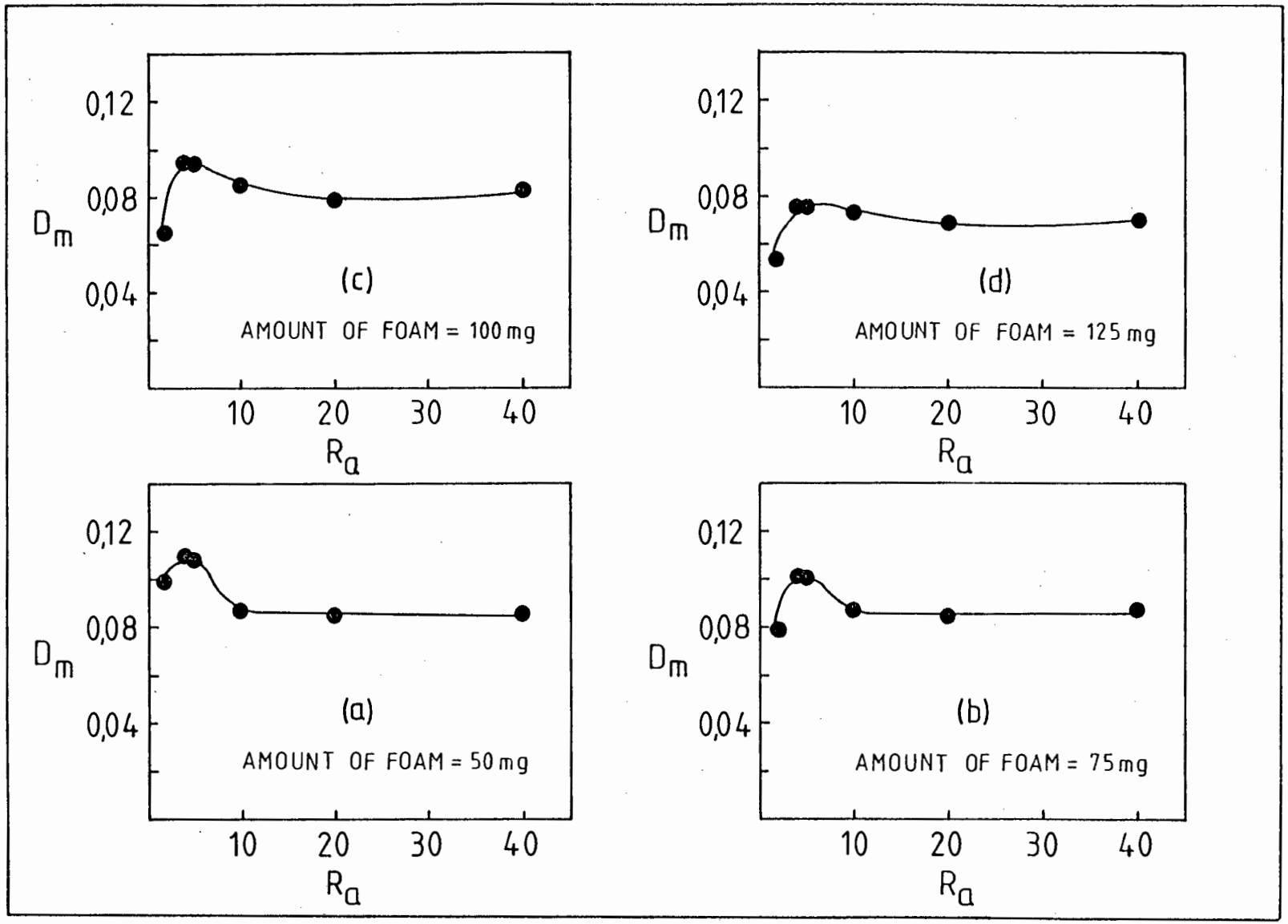


FIGURE 4.11 The Effect of R_a upon the foam's capacity for Platinum. The 1.0M HCl solutions used contained 100 ppm Platinum. The solution temperatures were maintained at 25°C. A different mass of foam was used for each set of experiments.

In Figure 4.12, for the experiments in which $R_a \leq 5$, the R_f values are all very similar and we note that $2 < R_f < 3$. At $R_a = 10$, however, a significant increase in R_f values occurs and this change is more dramatic the smaller the mass of foam. At some stage as we increase R_a, R_f reaches a limiting value of approximately 5. From Figure 4.12 we see that the larger the mass of foam the greater R_a has to be before R_f approaches this limiting value.

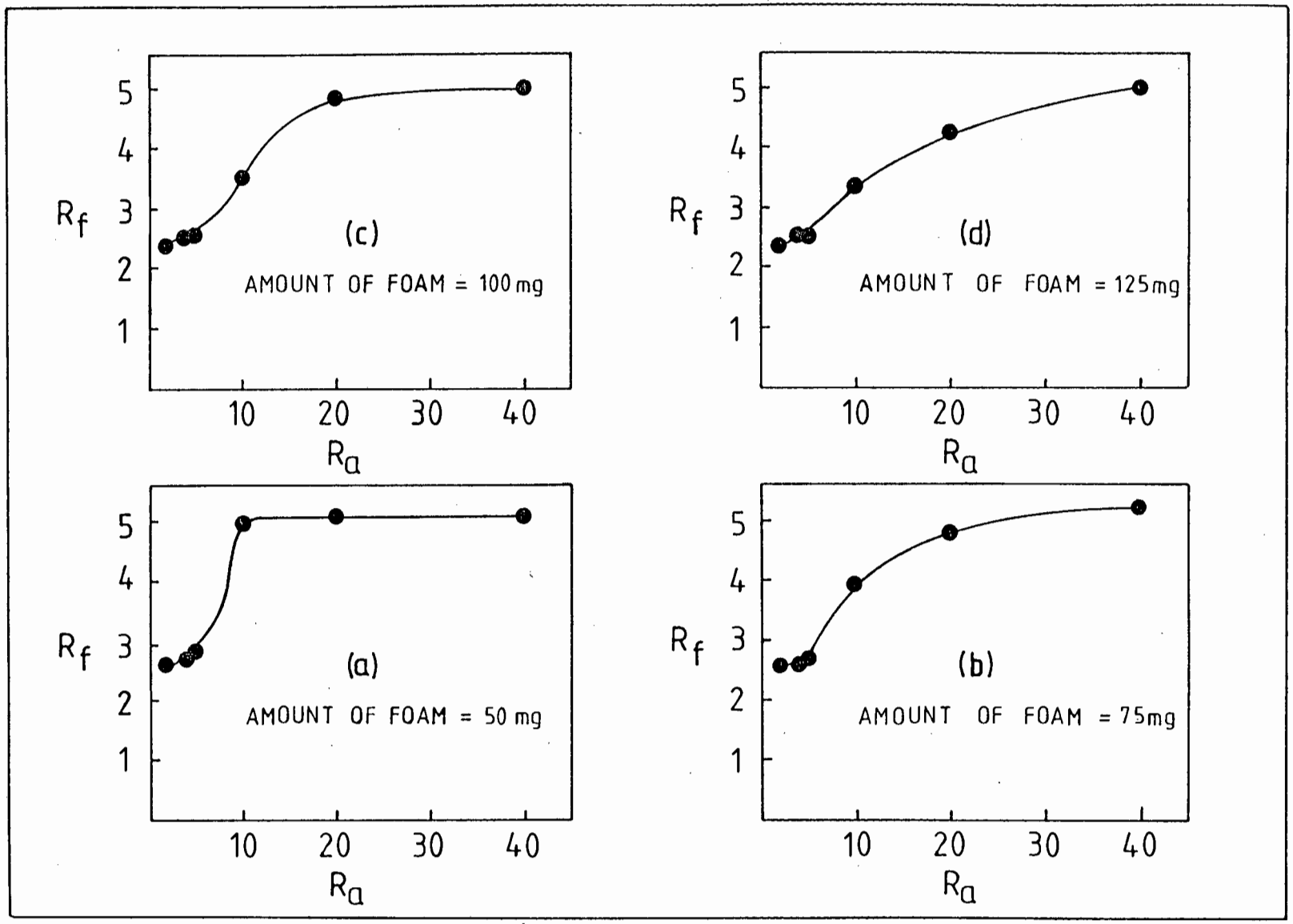


FIGURE 4.12 The Effect of R_a upon R_f. The 1.0M HCl solutions used contained 100 ppm Platinum. The solution temperatures were maintained at 25°C. A different mass of foam was used for each set of experiments.

CHAPTER 5

CHAPTER 5

5.1 The Extraction of Platinum by Polyurethane Foams from Solutions containing Base Metals

The occurrence of large amounts of base metals in the majority of PGM ore bodies, led us to examine the feasibility of selectively extracting platinum as its stannous chloride complex, from solutions containing a variety of base metals, using polyurethane foams.

The potential of this method for concentrating platinum and separating it from base metals is based on two facts. Firstly, it is generally accepted, that the trichlorostannato ligand only forms stable complexes with the PGMs and not with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). Secondly, most of the base metals we are concerned with, viz., Ni(II), Co(II) and Cu(II) do not extract into the polymer as their chlorides[47]. Fe(III) however, as $FeCl_4^-$ is known to sorb into foams[2,8]. No sorption study of zinc chloride had previously been undertaken.

To solutions containing the desired amounts of hydrochloric acid, platinum, tin(II) chloride and base metals, we added known excess quantities of foam. The large quantities of polyurethane (500mg) ensured the almost complete extraction of the noble metal from solution.

According to Table 5.1, essentially all of the platinum and less than 1.0% of the base metals, Fe(II), Co(II), Ni(II) and Zn(II) are extracted from solutions at different hydrochloric acid concentrations. Cu(II) being the exception, extracts into the foam to a significant extent.

Cationic Interferences % Metal Extracted						
[HCl]/M	Pt(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
1.0	> 99.5	-0.4	0.1	-1.1	7.2	0.0
2.0	> 99.5	-0.1	0.7	1.3	10.5	-0.1
3.0	> 99.5	-0.4	0.7	0.6	9.9	1.8
4.0	> 99.5	0.0	0.1	-1.1	9.9	1.2

Table 5.1 The extraction of Platinum from solutions containing base metals. Experimental conditions : Volume of Solution = 100ml, Initial [Pt] = 100 ppm, R_a = 10, [HCl] is varied and the amount of foam used = 500mg

5.2 The Extraction of Platinum by Polyurethane Foams from Solutions containing different anions

The smelting and pressure leaching procedures, used in extracting the noble metals from the ore (Figure 1.2), results in a variety of different anions being present in the ore concentrate. If an attempt is to be made at concentrating and separating the PGMs, using stannous chloride and polyurethane foams, these anions are likely to be present and their effect must be considered.

Anionic interferences of NO_3^-, SO_4^{2-} and ClO_4^- were investigated using their respective acids. The same experimental conditions of temperature, initial Sn:Pt ratio, platinum concentration and volume of solution were used in both the base metal and the anion interference studies.

Essentially all the platinum was extracted from solutions containing either the sulphate or perchlorate anion. If the aqueous phase contains sufficient nitrate ions, the percentage of platinum extracted is well below 100%. Refer to Table 5.2.

Anionic Interferences			
	1.0M SO_4^{2-}	1.0M NO_3^-	1.0M ClO_4^-
% Pt extracted	99.9	87.2	99.8

Table 5.2 The Extraction of Platinum from Solutions containing various Anions

Experimental conditions : Volume of solution = 100ml, Initial [Pt] = 100 ppm, R_a = 10, [HCl] = 1.0M and the amount of Foam used = 500mg

5.3 The Recovery of Platinum and Tin from Loaded Foams and their Separation

The viability of this method of extracting platinum from aqueous solutions is dependent on the costs of the necessary chemicals. The tin(II) chloride which is responsible for converting the platinum into its extractable form is the most expensive chemical component. For this reason our attention has been focused on the methods by which we could recover both platinum and tin from the foam and then separate the two.

In order to release platinum and tin from a loaded foam a suitable solvent may be used as a stripping agent. The disadvantage of using stripping agents such as hydrogen peroxide and ethanol is that pure aliquots must be continually passed through the foam until the platinum and tin

have been quantitatively eluted. This results in a significant dilution of the platinum concentrate.

Considering the low cost of the foam, the method of solubilising the loaded polyurethane with small quantities of warm concentrated HNO_3 appeared to be the most advantageous.

Of all the mineral acids used in attempting to dissolve loaded polyurethanes, only concentrated nitric acid was successful. In the first attempt to solubilise loaded foams use was made of teflon lined stainless steel digestion bombs. Small volumes of concentrated HNO_3 were added to the teflon cups containing the foam. The teflon cups were then placed inside their steel casings and heated in an oven at $120^{\circ}C$ for 6 hours.

In a set of experiments in which the digestion bombs were employed, the quantities of tin and platinum determined on a loaded foam by the change in solution concentration, were compared to values obtained when the dissolved foam itself was analysed. Table 5.3 shows that a mass balance exists for Pt,i.e. the quantity of platinum determined by difference corresponds closely to the amount of platinum found in the dissolved foam sample. This is not the case for tin where we see no detectable quantities in the solubilised foam solutions.

R_a	Amount of Metal in Foam determined by difference (mg)		Amount of Metal in Foam determined from dissolved foam (mg)	
	Pt	Sn	Pt	Sn
2	5.7	8.0	5.6	0.0
4	6.2	9.2	6.2	0.0
5	6.0	10.6	5.9	0.0
6	5.8	11.0	5.8	0.0
8	5.2	11.5	5.2	0.0
10	4.7	11.4	4.6	0.0
20	4.7	11.4	4.6	0.0
40	4.7	11.4	4.7	0.0

Table 5.3 Mass Balance check for Platinum and Tin.

Experimental conditions: Volume of solution = 100ml, Initial [Pt] = 100ppm, R_a varies, [HCl] = 1.0M and the amount of Foam used = 50mg.

A close examination of the teflon cup of the digestion bomb, revealed a white deposit which we believed was some form of an insoluble tin nitrate. The inconvenience of using digestion bombs and the lengthy procedures they involved seemed unnecessary. A simple method was adopted to determine the platinum associated tin absorbed by the foam. It simply involved dissolving the polymer in warm nitric acid in an Erlenmeyer flask. Once the foam had been completely solubilised the HNO_3 was boiled off and concentrated hydrochloric acid added to dissolve the tin as a chloride.

As is evident from Table 5.4 we were able to achieve a satisfactory mass balance for both the platinum and tin.

R_a	Amount of Metal in Foam determined by difference (mg)		Amount of Metal in Foam determined from dissolved foam (mg)	
	Pt	Sn	Pt	Sn
2	5.7	8.2	5.6	8.1
4	6.8	9.3	6.2	9.1
5	6.0	10.7	6.0	10.6
6	5.8	11.0	6.0	10.7
8	5.2	11.4	5.2	11.4
10	4.6	11.4	4.6	11.4
20	4.8	11.4	4.7	11.3
40	4.8	11.4	4.8	11.3

Table 5.4 Mass balance check for Platinum and Tin.
Experimental Conditions: Volume of solution = 100ml, Initial [Pt] = 100ppm, R_a varies, [HCl] = 1.0M and the amount of foam used = 50mg

A distillation process used by Lehmann[44], the details of which are given in the experimental section, was adopted in an attempt to separate the platinum and tin from a solution containing these metals and solubilised foam. Table 5.5 shows that as we had anticipated, all the tin and no platinum had distilled across. Unexpectedly, however, we could only account for less than 50% of the platinum in the original solubilised foam solution.

	Amount of Metal in the solubilised Foam Solution (mg)		Amount of Metal in the Distillate (mg)	
	Pt	Sn	Pt	Sn
Predicted Value	10.0	0.0	0.0	10.0
Determined Value	4.5	0.0	0.0	9.9

Table 5.5 Separation of Platinum and Tin by Distillation

Experimental conditions: Amount of Pt = 10mg, Amount of tin = 10mg and the Amount of foam used = 50mg

It is unlikely that the platinum volatilised on heating and so we must assume that the metal has remained in the solubilised foam solution, but due to matrix effects is not completely accounted for by AAS. The importance of being able to separate and quantitatively determine the platinum and tin deserves further research.

CHAPTER 6

CHAPTER 6

6. DISCUSSION AND CONCLUSIONS

The preliminary experiments of the extraction of cobalt isothiocyanate, from water/ethanol media into polyurethane foam, facilitated the design and construction of a suitable extraction apparatus. These studies also provided us with some insight into the general thermodynamic and kinetic behaviour of foams, as regards their sorption of metal anions from solution.

A state of true equilibrium where a plot of LnK_d vs $^1/T$ is linear, has been shown to exist for the system,

$$2K^+ + Co(NCS)_4^{2-} \rightleftharpoons \overline{K_2Co(NCS)_4^{2-}}$$

if the ratio of foam mass (mg) : $Co(NCS)_4^{2-}$ mass (mg) is sufficiently large. As observed previously, curves A and B in Figure 3.1 are linear for the temperature interval studied and thus indicate a state of true equilibrium. Curves C and D on the other hand, which represent a situation of lower foam mass : $Co(NCS)_4^{2-}$ mass ratio, deviate from linearity at temperatures below 45^oC

Using the following reasoning one may attempt to explain why true equilibrium does not exist at all temperature conditions, where we have a low foam to $Co(NCS)_4^{2-}$ mass ratio. The lower the temperature, the greater is the tendency for the $Co(NCS)_4^{2-}$ to sorb into the foam. Now if there is insufficient foam present in the solution, it rapidly reaches capacity and cannot accommodate any more cobalt. We therefore have a situation in solution, where the thermodynamic conditions are such, that the cobalt species have the potential to extract but have no more foam sites onto which to do so.

Kinetics data treated with a first order reaction equation, has resulted in the generation of a series of curved graphs over a time interval of 15 minutes. Refer to Figure 3.4. When, however, the data is plotted for the initial 100 seconds of the sorption process, the linear sections of the curves become apparent (Figure 3.3). It would appear that the higher the foam mass : cobalt mass ratio, the more extensive these initially linear sections become.

When the kinetics data is treated with the second order reaction equation, we have much the same results as those obtained from the first order treatment. It should be noted that linear sections are more extensive in curves obtained by the second order reaction treatment of the data. The linear sections observed for both treatments, may represent a pseudo first or second order reaction. Departures from linearity, could indicate a situation in which diffusion becomes the rate determining process. This being the case, diffusion is likely to complicate attempts to interpret the kinetics data in terms of the reaction order and mechanisms of sorption.

A rigorous study of the kinetics of sorption for the platinum-tin complexes, into polyurethane foam, was not undertaken for two reasons. Firstly, the kinetics apparatus (Figure 7.4) was not appropriate, because the UV-VIS spectrophotometric method of analysing for platinum was unsuitable. The absorptiometric determination of platinum requires that the noble metal be complexed with tin(II) chloride[43] and it is the Sn : Pt molar ratio of the solution that affects ε. If polyurethane foam is added to a platinum-tin(II) chloride solution, it extracts various Sn:Pt complexes and so alters the Sn:Pt ratio in solution and therefore changes ε. For the continuous quantitative determination of any chemical species by UV-VIS spectrophotometry, ε must remain constant. The other reason for not

undertaking a rigorous kinetics study of the foam's sorption of platinum, was that as in the cobalt case, diffusion is likely to complicate attempts to establish the order of reaction and no further information concerning mechanisms of sorption is likely to be obtained.

The rate and extent to which platinum is extracted from solutions by polyurethane foams, is determined by a number of factors which are considered here. Results have clearly shown that up to a certain maximum value, the higher the initial platinum concentration of the solution, the greater is both the rate of sorption and capacity of the foam for the metal. Refer to Figures 4.3 and 4.4. Identical trends were observed for the cobalt study. A diffusion process generated by a concentration gradient between solution and foam may be expected to determine both the rate and the extent to which the sorption of platinum occurs. Diffusion, if it operates, is likely to occur simultaneously with the mechanism or mechanisms of extraction.

Like many other chemical reactions whose velocities are increased with higher temperatures, so it is with the sorption of platinum into the polyurethane foam. This fact supports the idea of a diffusion process operating within the polymer, because we know from other examples that diffusion rates increase with a rise in temperature.

The diminished capacity of the foam associated with higher temperatures, has been previously explained in terms of the thermodynamic expression $\mathrm{Ln}K_d \propto \frac{-\Delta G}{RT}$. The fact that a large decrease in free energy ΔG occurs during the sorption process, means that as the temperature of the solution is raised K_d must decrease i.e. capacity is diminished.

Although we have not determined the effect of temperature on the various platinum species in solution, it is quite likely that there will be

a shift in their equilibria as the temperature is varied. It is also possible that at higher temperatures, more of a non-extractable type of platinum complex could be present in solution. This would also explain our capacity-temperature relationship.

Another factor found to affect the foam's capacity for platinum was the hydrochloric acid concentration of the solution. Trends observed in Figure 4.5 are explained here, in terms of the effect of acid strength upon the sorption 'sites' in the foam and on the platinum species in the aqueous phase.

Considering three possible operative mechanisms of extraction namely, cation chelation, ligand addition and anion exchange, we expect that an increase in hydrochloric acid concentration would lead to the polyurethane having a larger sorbtive capacity. An increase in acid strength should lead to a greater degree of protonation of nitrogen atoms in the crosslinks of the foam and of oxygen atoms in the polyether sections of the polymer. These protonated sites could then function as anion exchange sites for the platinum complexes. Assuming the cation chelation mechanism operates, then an increase in the number of H_3O^+ ions in the helical structure of the foam (sorption 'sites') will result from an increase in the HCl concentration of the solution.

As the experimental results have shown (Figure 4.5) there is no simple direct relationship between HCl concentration and the sorbtive capacity of the foam for platinum. It would appear that the biggest factor affecting the extraction of platinum by the foam, is the nature of the platinum-tin complexes, which are in turn affected by the acid strength of the solution.

The UV-VIS spectra of the platinum-tin(II) chloride complexes

observed in Figures 3.7 - 3.9 indicate a marked change in character as the hydrochloric acid concentration changes from 1.0 - 2.0M. Species are however, relatively unchanged in acid concentrations of 2.0 - 4.0M, based on the fact that these spectra are almost superimposable.

Changes in the nature of the platinum complexes observed as a function of [HCl], may be explained in terms of the equilibria proposed by Young *et al.*[27] shown below.

$$[PtCl_3(SnCl_3)]^{2-} + SnCl_3^- \rightleftharpoons [PtCl_2(SnCl_3)_2]^{2-} + Cl^- \qquad (1)$$

$$[PtCl_2(SnCl_3)_2]^{2-} + 3SnCl_3^- \rightleftharpoons [Pt(SnCl_3)_5]^{3-} + 2Cl^- \qquad (2)$$

Any increase in the hydrochloric acid concentration will cause a shift in these equilibria to the left because of the increased chloride concentration of the solution. Referring to Figure 4.5, as the HCl concentration is increased from 0.50 - 0.75M the platinum reaches its maximum extraction value. This marked change in platinum extraction values corresponds to the significant changes in the platinum species, observed in the UV-VIS spectra, as HCl concentrations are varied in a similar range. Where we see little change in the nature of the platinum complexes (2.0 - 4.0M HCl) we note in Figure 4.5 that platinum and tin sorption is essentially constant.

The platinum and tin extraction trends obtained by varying [HCl] and $[H^+]$ were compared (Figures 4.5 and 4.6) and appear to be similar. This suggests that $[H^+]$ rather than $[Cl^-]$ has the largest effect upon the platinum species in solution and that hydrolysis may, to some extent affect these complexes. If hydrolysis of the platinum-tin halide compounds can occur as Kukushkin's work shows[50], then partial hydrolysis of the trichlorostannato-platinum complexes, in solutions which have either low H^+ or Cl^- concentrations may occur. As an example the $[Pt(SnCl_3)_5]^{3-}$ complex may undergo hydrolysis as shown below.

$$[Pt(SnCl_3)_5]^{3-} + 5H_2O \rightleftharpoons [Pt(SnCl_2OH)_5]^{3-} + 5Cl^- + 5H^+ \quad (1)$$

$$[Pt(SnCl_2OH)_5]^{3-} + 5H_2O \rightleftharpoons [Pt(SnClOH_2)_5]^{3-} + 5Cl^- + 5H^+ \quad (2)$$

$$[Pt(SnClOH_2)_5]^{3-} + 5H_2O \rightleftharpoons [Pt(SnOH_3)_5]^{3-} + 5Cl^- + 5H^+ \quad (3)$$

If the more hydrolysed species are preferably extracted into the polyurethane, then we can expect a decrease in platinum sorption as the $[H^+]$ increases.

The effect of HCl concentration upon the stannous chloride species in solution, shown in Figure 6.1, must be taken into consideration when trying to explain our platinum and tin extraction trends. It is significant that the concentration of the only stannous chloride ion thought to complex with the platinum, $SnCl_3^-$, varies significantly between 0.5 and 2.0M HCl but is relatively constant between 2.0 and 4.0M. The changes in the trichlorostannato ligand concentration, which must affect the nature of the platinum complexes, may explain the changes in platinum species observed in the UV-VIS spectra.

Both changes in the number of sorption 'sites' in the foam and the platinum complexes in solution, resulting from varying [HCl], are likely to have determined the extraction trends seen in Figures 4.5 and 4.6.

In experiments to test if the cation chelation mechanism operates between the foam and the platinum-tin(II) chloride complexes in solution, we found that the alkali metal cations, Li^+, Na^+ and K^+ have a depressive effect on the extraction of platinum (Figure 4.7). This is apparently related to ionic size where the larger the size of the cation in solution, the less platinum is taken up by the foam. Our cation size-sorption trend is completely the opposite to that predicted by the CCM. According to

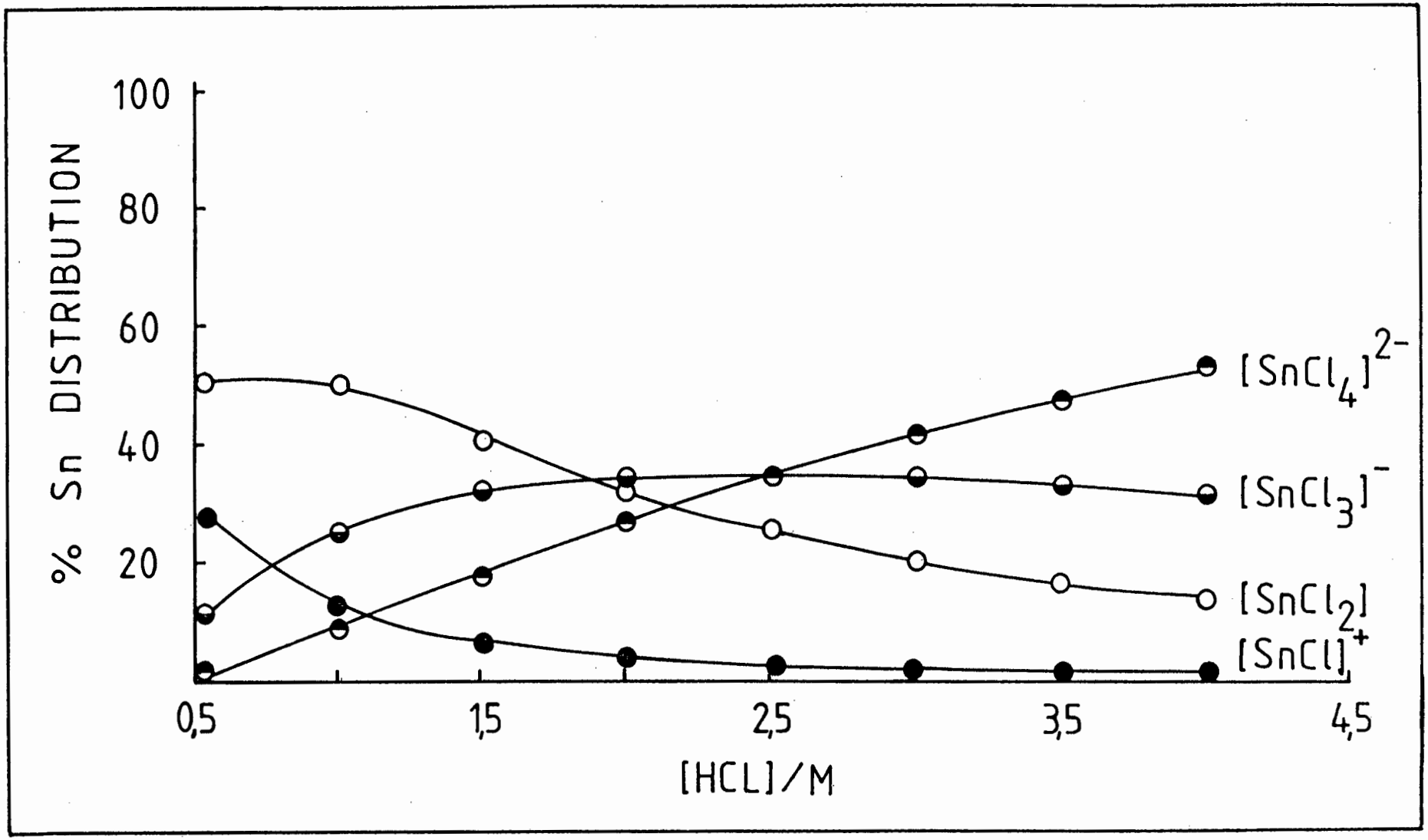


FIGURE 6.1 The Distribution of tin(II) chloride complexes as a function of HCl concentration

Hamon[9] maximum anion extraction is related to the order $K^+ > Na^+ > Li^+$ whereas in our case the order was $Li^+ > Na^+ > K^+$.

Two important points emerge from Figure 4.8. Firstly, the R_f values for each different cation examined are reasonably consistent as we vary their concentrations (Table 6.1) and secondly the average R_f values for each different cation examined are very similar (Table 6.2).

Concentration moles/dm^3 KCl/NaCl/LiCl	R_f for foam equilibrated in KCl soln.	R_f for foam equilibrated in NaCl soln.	R_f for foam equilibrated in LiCl soln.
0.25	4.48	4.60	4.34
0.50	4.45	4.56	4.56
0.75	4.88	4.93	4.61
1.00	4.64	4.72	4.48
1.25	4.49	4.67	4.63
1.40	4.45	4.51	4.62

Table 6.1 R_f values for foams equilibrated in Platinum/Stannous Chloride solutions containing either KCl, NaCl or LiCl.

Cation	Average R_f value
K^+	4.57
Na^+	4.67
Li^+	4.54

Table 6.2 Average R_f values for foams equilibrated in Platinum/Stannous Chloride solutions containing either KCl, NaCl or LiCl.

Based on the assumption that the R_f value of the foam reflects the nature of the platinum-tin complexes in solution, the similar R_f values we have observed, indicate that the alkali metal cations have a minimal effect on the species in solution.

If we accept that the cations have little effect on the aqueous phase, besides altering the ionic strength of the solution, we can deduce that there must be some cation-foam interaction that reduces the polyurethane's ability to accommodate platinum.

The specific nature of this cation-foam interaction is difficult to determine and we can only make suggestions. It is possible that foam immersed in only acid solutions containing platinum and stannous chloride, does not extract the hydronium ion (H_3O^+) in its polyether chains as predicted by the CCM, but instead the H^+ ions in solution protonate nitrogen atoms in the urethane and other crosslinkages. These protonated sites then operate as anion exchange sites for the platinum complexes. Figure 6.2 represents a very simplified view of a section of foam in which protonation alone, provides two platinum complexes with sorption 'sites'.

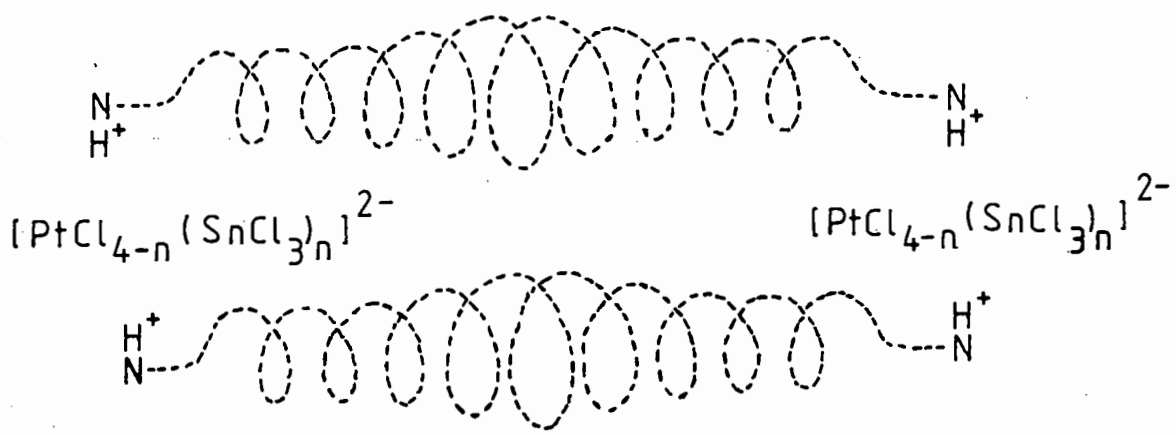


Figure 6.2 Simplified view of foam showing Platinum complexes attached to protonated 'sites'. Furthermore, only one particular platinum complex is considered.

For a foam immersed in solutions containing sufficient quantities of alkali metals, HCl, platinum and stannous chloride, we are likely to have the CCM playing a more significant role. In Figure 6.3 we see three platinum compounds sorbed by the foam at two different types of 'site'. The electrical repulsion experienced by these anions may result in potential 'sites' remaining vacant.

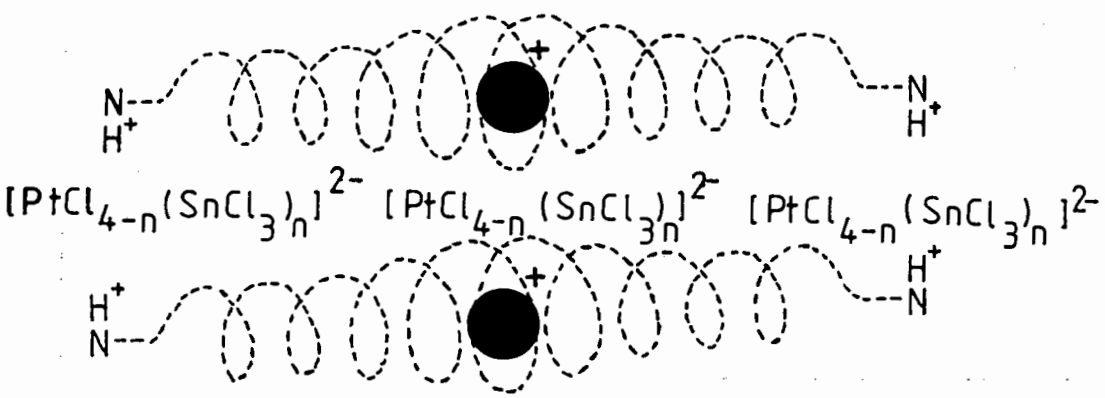


Figure 6.3 Simplified view of foam showing Platinum complexes at protonated and CCM 'sites'

In Figure 6.4 we have assumed that the CCM 'sites' provide a stronger attraction for the platinum anions than do the protonated 'sites'. The forces of repulsion experienced between proximal anions, may prevent other negatively charged complexes sorbing into the foam, adjacent to the platinum complex which is situated at a CCM 'site'. Refer to Figure 6.4. This could explain the depressive effects of the alkali metal cations on the extraction of platinum.

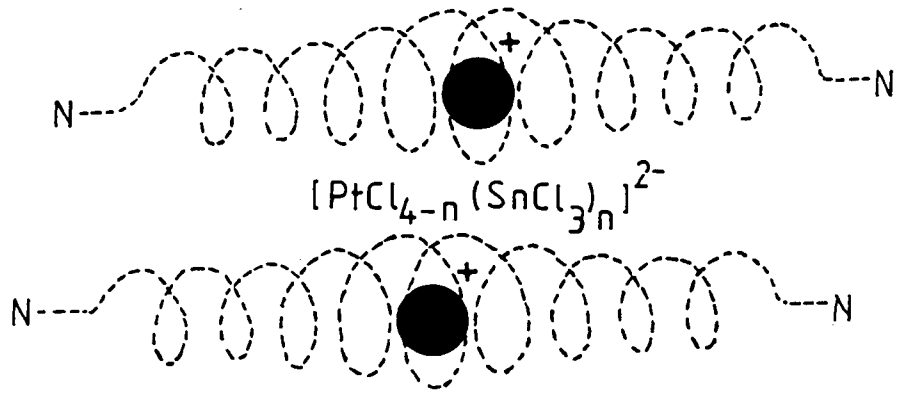


Figure 6.4 Simplified view of foam showing Platinum complex at a CCM 'site'

The order of best fit for alkali metal cations into the polyether section of the foam being $K^+ > Na^+ > Li^+$, it is possible that the extent to which the CCM operates is also related to the same order. This would in terms of the previous discussion, explain why the depressive effect of the cations on the platinum extraction is related to $K^+ > Na^+ > Li^+$.

As R_a (Sn:Pt molar ratio of the solution) increases so a distribution in favour of the $[Pt(SnCl_3)_5]^{3-}$ species in solution is expected. The fact that rates of platinum extraction are generally greater at $R_a = 5$ than they are at $R_a = 2$ (Figures 4.9 and 4.10), suggests that the complex $[Pt(SnCl_3)_5]^{3-}$ is more rapidly extracted into the foam than are other complexes of the form $[PtCl_{4-n}(SnCl_3)_n]^{2-}$ (n = 1 to 4).

In order to explain how the initial R_a effects R_f (the average Sn:Pt molar ratio of the complexes in the foam) and the capacity of the foam for

platinum, the following postulates were proposed:

(1) the quinqueco-ordinated platinum complex $[Pt(SnCl_3)_5]^{3-}$, which is bulky is likely to be more hydrophobic than other species such as $[PtCl_{4-n}(SnCl_3)_n]^{2-}$ (n = 1 to 4) and therefore preferably sorbed into the foam

(2) the square-planar complexes and others of lower Sn:Pt stoichiometry havinga 2(-)charge utilize 2 sorption sites in the foam. By the same token the trigonal bipyramidal form $[Pt(SnCl_3)_5]^{3-}$ having a 3(-) charge will require 3(+) charges to achieve electrical neutrality and

(3) the smaller the mass of foam the fewer sorption sites exist for anions to extract into.

In Figure 4.11 we see that maximum platinum extraction occurs at R_a values of between 4 and 5. Between R_a values of 5 and 10 the amount of platinum sorbed decreases and for the R_a interval 10-40 the noble metal extraction is essentially constant.

As R_a increases so the equilibrium $[PtCl_{4-n}(SnCl_3)_n]^{2-} \rightleftharpoons [Pt(SnCl_3)_5]^{3-}$ shifts to the right. If we accept that all of these different forms of the platinum complex are sorbed into the foam, then we can rationalise why an increase in R_a above 5 causes a decline in the amount of platinum extracted. Because the $[Pt(SnCl_3)_5]^{3-}$ complex utilizes three sorption sites and $[PtCl_{4-n}(SnCl_3)_n]^{2-}$ only two to satisfy electrical neutrality, the former is likely to consume more 'sites' within the foam. If there are a limited number of 'sites' (i.e. a small quantity of foam), then an increase in R_a will lead to a decrease in platinum extraction.

Varying R_a values from 2 - 40 with different quantities of foam, 50, 75, 100 and 125 mg we see the effect this has on R_f (Figure 4.12). As R_a increases we expect the Sn:Pt ratio of the platinum complexes in solution will increase and expect this to result in an increase in R_f values. At

R_a < 10, R_f values for all four masses of foam are approximately the same. At R_a = 10 we see significant increases in R_f, the most significant being for the smaller masses of foam. At R_a = 40 all the R_f values are approximately equal to 5.

In a solution having R_a = 10, it is likely that we will have a mixture of Sn:Pt species with the 5:1 complex probably predominating. The $[Pt(SnCl_3)_5]^{3-}$ complex is preferentially sorbed (proposition 1) and if there are sufficient 'sites' remaining, the square planar complexes and species of lower Sn:Pt stoichiometry will then be accommodated by the polymer. We see at R_a = 10 in the case for which 50mg of foam was used (Figure 4.12(a)) that R_f = 5. This suggests that only sufficient sites existed in the polyurethane for the 5:1 species. As we increase the mass of foam so more of the lower Sn:Pt complexes sorb and this will reduce the average Sn:Pt ratio of the complexes on the foam (R_f).

Under our solution conditions the $SnCl_3^-$ ligand only forms stable complexes with the platinum and not the base metals. The polyurethane foam extracts the platinum in this form, but generally does not sorb the base metal chloro complexes. Results in Table 4.1 demonstrate the selectivity of this method for the extraction of platinum. Small amounts of copper however, have been shown to co-extract into the solid organic phase.

Work completed by Braun and Huszar[47] has shown that copper in its bivalent state is not extractable into polyurethane foams from hydrochloric acid media. The limited co-extraction of copper with platinum may be explained in two ways. Firstly in the presence of stannous chloride, bivalent copper may form complexes of the type $[Cu(SnCl_3)_nCl_{4-n}]^{2-}$ which are extractable into the polyurethane. The other alternative is that Cu(II) is reduced to its univalent state as shown below,

$$2Cu^{2+} + Sn^{2+} \longrightarrow 2Cu^{+} + Sn^{4+}$$

and copper as its Cu(I) chloride is extractable into the foam. No attempts were made to find out in what form the copper extracts.

Unexpectedly the Fe(III) did not extract into the foam as its $FeCl_4^-$ complex. We reasoned that because the solution only contained a 100 ppm Fe(III) and Sn(II) in excess, most of the Fe(III) could have been reduced to its unextractable bivalent state as shown below.

$$2Fe(III) + Sn(II) \longrightarrow 2Fe(II) + Sn(IV).$$

The presence of major quantities of Fe(III) in the platinum-stannous chloride solutions, is therefore likely to result in the iron being co-extracted with the platinum. The extraction of platinum by foams from solutions containing large concentrations of base metals was not examined.

In the anion interference study it was found that only NO_3^- caused a decrease in the percentage platinum extracted. The nitrate anion in concentrated acid solutions is known to be a strong oxidising agent, and it is quite likely that at the concentrations of nitric acid we were using, significant quantities of Sn^{2+} were oxidized to Sn^{4+}. Tin in its tetravalent state does not complex with the platinum.

Solubilising the foam with warm nitric acid would appear to be the most convenient, efficient and cost effective method of recovering platinum from the loaded foams. The demonstration of mass balance for platinum and tin has increased our confidence in our measurements.

The separation of tin from platinum by distilling the tin over as a volatile bromide ($SnBr_4$) was achieved. The one problem encountered with this procedure being that we were unable to account for all the platinum. Because we determined the platinum by AAS, it is possible that the sulphuric

acid used in the distillation procedure, could cause severe matrix effects that resulted in the depression of the absorbance signal for platinum.

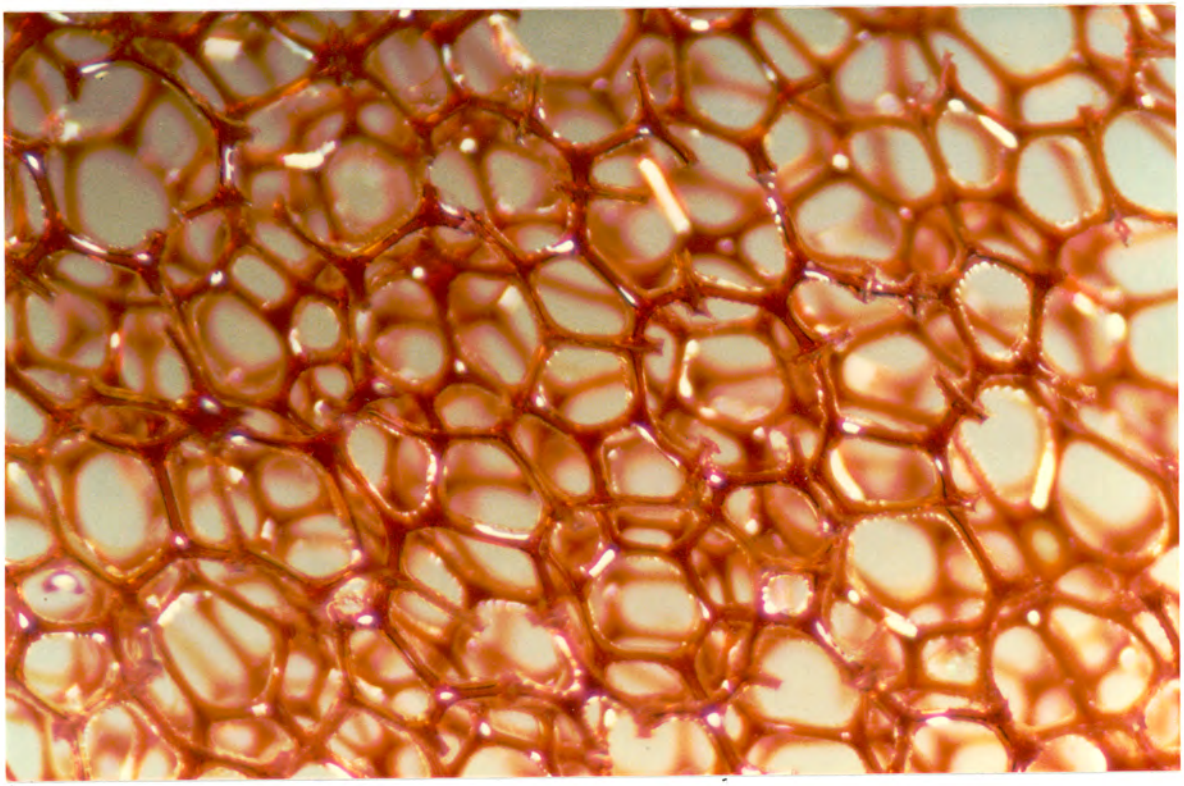
CONCLUSION

Polyurethane foams which are both cheap and readily available, have proved to be an extremely successful media for the extraction of platinum, for a number of reasons. The polymer has displayed a large capacity for the noble metal. At optimum conditions (i.e. temperature = 25^{o}C, Sn:Pt = 5:1, HCl concentration of 0.75M and an amount of foam equivalent to 100mg) we achieved a maximum capacity value of 0.68 moles of Pt per kg of foam.

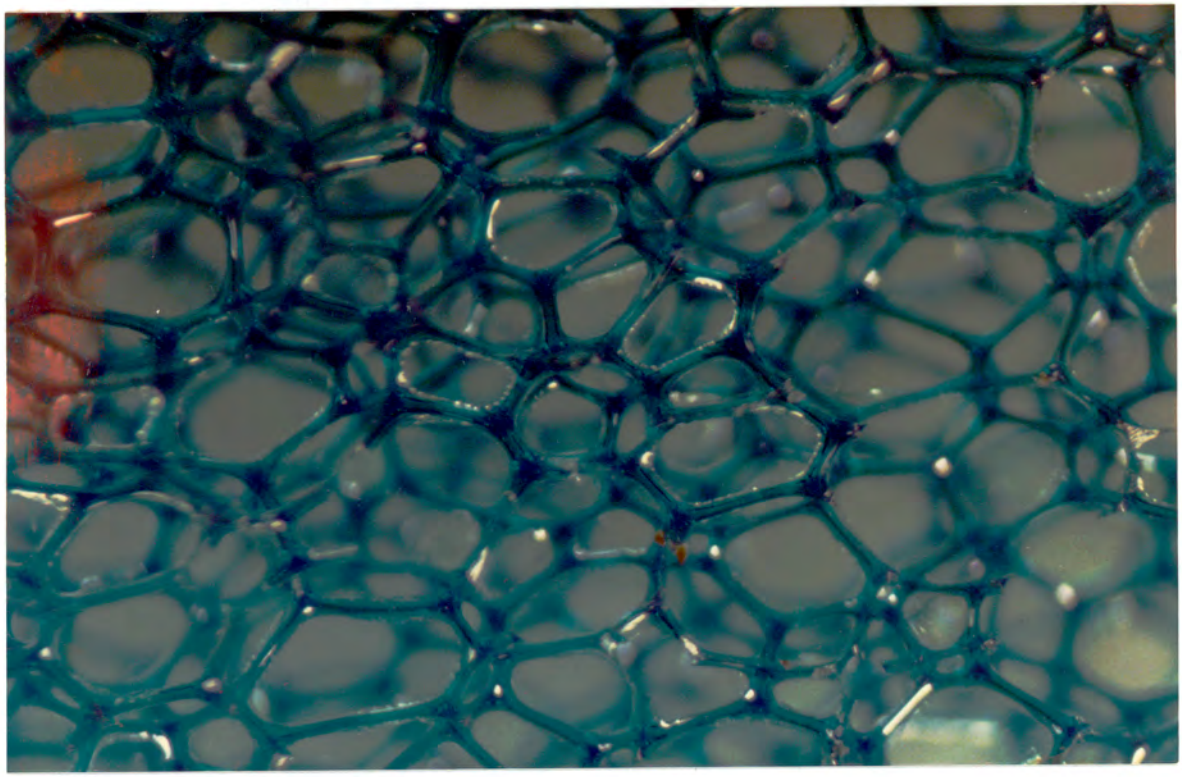
This study has allowed us to determine the effects of various parameters upon the foam's ability to extract platinum from aqueous hydrochloric acid solutions. We have shown that platinum can be quantitatively and selectively extracted from solutions containing low concentrations of the precious metal and an assortment of base metals.

The recovery of platinum and tin from loaded foams and their separation has, to a large extent been achieved. The method involving the solubilising of the foam has proved to be the most convenient and effective method of retrieving the metals.

The kinetics study of the cobalt sorption process proved inconclusive. Photographs of the loaded foams taken through a microscope, shown overleaf, illustrate how the extracted chemical compounds are distributed throughout the body of the foam, a fact that confirms absorption rather than adsorption occurs. The effects of temperature and initial metal concentration, on the capacity of the foam and the rates of extraction suggest that diffusion may be the rate determining process.



PHOTOGRAPH 1 A magnified view of a foam loaded with the platinum-tin complexes



PHOTOGRAPH 2 A magnified view of a foam loaded with the $Co(NCS)_2^{2-}$ complex.

The extracted species are all apparently anionic and a number of mechanisms such as, solvent extraction, anion exchange, cation chelation and ligand addition may be responsible for the observed sorption phenomena. The attempt at determining the reaction order for the extraction of cobalt by the foam was inconclusive. We had hoped that a knowledge of the reaction order would have yielded some information about the sorption process.

CHAPTER 7

CHAPTER 7

EXPERIMENTAL

7.1 Chemicals, Reagents and Glassware

All reagents and chemicals used for this experimental work were analar grade and were obtained from various suppliers. The K_2PtCl_4 and $SnCl_2 \cdot 2H_2O$ used were produced by Johnson Matthey Chemicals Limited, Wadeville and Hopkins and Williams Ltd., England respectively. $La(NO_3)_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, zinc metal, LiCl, NaCl and KCl were supplied by E. Merck, Darmstadt.

The $HClO_4$ supplied by BDH Chemicals, England and the HCl, H_2SO_4 and HNO_3 obtained from E. Merck, Darmstadt were accurately standardised with sodium tetraborate.

Commercial grade nitrogen supplied by Afrox, Cape Town was purged of oxygen by passing it through a chromous chloride solution and then distilled water before use[40].

Double-distilled water which was initially boiled for twenty minutes to remove dissolved carbon dioxide and oxygen was allowed to cool under nitrogen. It was then stored in a glass aspirator fitted with a nitrogen inlet. This water was used in the preparation of all aqueous solutions. All solutions prepared for extraction experiments were again purged with nitrogen for thirty minutes prior to the addition of the $SnCl_2 \cdot 2H_2O$.

Sheets of polyether polyurethane foam of three different densities were obtained from Flexaire Foams, South Africa. These sheets were first cut into cubes, washed with Tepol detergent and then thoroughly rinsed. The cubes

were subsequently soaked in 0.5M HCl for 72 hours, followed by multiple rinses with deionised water until the rinsing water was neutral to pH indicator paper. Finally the foam cubes were allowed to stand in acetone overnight and then oven dried at 50°C.

A mixture of A and B grade glassware was used. Tin solutions were dispensed with Gilson pipettes and the platinum and base metal solutions were transferred by A grade pipettes. All materials were weighed using Mettler and Sartorious four decimal place balances.

Microanalyses were performed on a Heraeus Universal Combustion Analyser, Model CHN-Micro, by Mr. W.R.T. Hemsted of the Department of Organic Chemistry, University of Cape Town.

7.2 Atomic Absorption of Platinum

Platinum stock solutions of 1000 ppm were prepared by dissolving solid K_2PtCl_4 into hydrochloric acid solutions of the appropriate concentration. Stock solutions of the releasing agent $La(NO_3)_3$ were made up with the necessary amount of HCl. Quantities of this solution were added to both samples and standards so that the final solutions had a La^{3+} concentration of 0.2%.

Two distinct sets of platinum standards were used. In the first type the standards were prepared in hydrochloric acid media, with concentrations ranging from 0.5 - 4.0M. The platinum concentration range used was 0-50 ppm. For the second set of standards, certain quantities of nitric acid dissolved foam were added. These standards also contained a platinum concentration in the range of 0-50 ppm. Additions of tin(II) to both types of standard were made, so as to match the ratios of the sample matrix with the standards. All samples and standards were run on the same day.

The Varian Techtron 70 atomic absorption spectrophotometer was used for all measurements. The strongly oxidising air-acetylene flame was used for the analysis of platinum together with the spectrophotometer settings shown in Table 7.1.

Lamp/Current/mA	:	10
Wavelength/nm	:	265.9
Slit Width/nm	:	0.2

Table 7.1 The Spectrophotometric settings used during the analysis of Platinum

The amount of platinum extracted into the foam was calculated as follows; before the extraction experiment begins a sample of the solution is taken and analysed. This is the initial platinum concentration. Samples taken at any stage after the extraction procedure has begun, are analysed and this value is subtracted from the initial value, to give the amount of platinum that has been extracted into the foam.

7.3 Atomic Absorption of Tin

Stannous chloride stock solutions of 1000 ppm were made up in 1.0M hydrochloric acid solutions. Fresh stock solutions were made up every 3 weeks.

A series of standards were prepared in the range of 0-100 ppm at the appropriate acid concentration. All samples and standards were run on the same day of preparation and standards were freshly made for each extraction.

All measurements were made on a Varian Techtron 70 atomic absorption spectrophotometer, using a strongly reducing air-acetylene flame.

Table 7.2 lists the spectrophotometric settings.

Lamp Current/mA	:	5
Wavelength/nm		286.3
Slit Width/nm	:	0.2

Table 7.2 The Spectrophotometric Settings used during the analysis of tin.

The amount of tin extracted into the foam was calculated as for the platinum case.

7.4 The Atomic Absorption of the Base Metals

Stock solutions of the base metals were prepared from their dried chlorides, by dissolving them in 1.0M hydrochloric acid. The concentrations of these solutions were accurately determined by atomic absorption using Spectrosol analar standards.

A series of base metal standards were prepared in the range 0-50 ppm at suitable acid concentrations. As always samples and standards were matched as closely as possible and were run on the same day of preparation.

Again use was made of the Varian Techtron 70 atomic absorption spectrophotometer and the air-acetylene flame to analyse for the base metals. Table 7.3 lists the spectrophotometric settings

Base metal	Lamp current/ mA	Wavelength/ nm	Slit Width/ nm
Fe	5	372.0	0.1
Co	5	304.4	0.2
Ni	5	232.0	0.2
Cu	3	324.7	0.2
Zn	5	213.9	0.1

Table 7.3 The spectrophotometric settings used for the analysis of base metals.

The amounts of base metal extracted into the foam were calculated as for the platinum and tin cases.

7.5 Ultraviolet-Visible Spectrophotometry of Platinum

Three sets of solutions each containing 100 ppm Pt had Sn:Pt ratios of 1:2, 1:5 and 1:10. Each set had four different hydrochloric acid concentrations of 1.0, 2.0, 3.0 and 4.0M. These solutions were kept under de-oxygenated nitrogen and allowed to reach equilibrium.

The spectra were run on 10 mm quartz cells containing the platinum-stannous chloride solution. Solutions in the sample and blank cells were similar in every respect except that the latter contained no platinum.

A Superscan 3 Varian Ultraviolet-visible spectrophotometer was used. Spectra were run between 300 and 600 nm using a slit width of 1.5nm and a scan speed of 200nm/min.

7.6 Ultraviolet-Visible Spectrophotometry of Cobalt

The cobalt chloride dissolved into the ethanol/water solutions to give the required cobalt concentration, was dessicator dried. Distillation

of ethanol at approximately 78°C was performed prior to its mixing with water, because the relatively pure ethanol has a strong tendency to absorb H_2O from the atmosphere.

The shrinkage in volume that occurs when water and ethanol are mixed, is due to the reduction of hydrogen-bond lengths by the ethanol. To avoid this shrinkage problem we adopted the following procedure. If a one l quantity of a 50:50 ethanol/water solution was required, we added the 500ml of pure ethanol first and then made up to volume with the distilled water. A period of time was allowed to elapse for shrinkage to occur and then distilled water was again added to make the solution up to volume.

The spectra were run on 10mm quartz cells containing the cobalt and potassium thiocyanate solutions. Solutions in the sample and blank cuvettes were similar in every respect except that the blank contained no cobalt.

A Superscan3 Varian Ultraviolet-visible spectrophotometer was used. Spectra were run between 400 and 700nm using a slit width of 1.5nm and a scan speed of 200nm/min. For the kinetics study the spectrophotometer was operated at the fixed wavelength λ_{max} = 618nm and time scans were either of 200 seconds or 200 minutes duration.

7.7 Potassium Iodate Oxidations

Potassium iodate solutions of the required concentration were made up by dissolving the oven dried solid into boiled-out distilled water.

The Erlenmeyer flask shown in Figure 7.1 was flushed with nitrogen prior to the addition of known volumes of tin(II) solution, 10ml of

degassed 5.0M HCl and the 10ml of chloroform. Potassium iodate was then added to the flask via the burette while the whole system is kept under nitrogen.

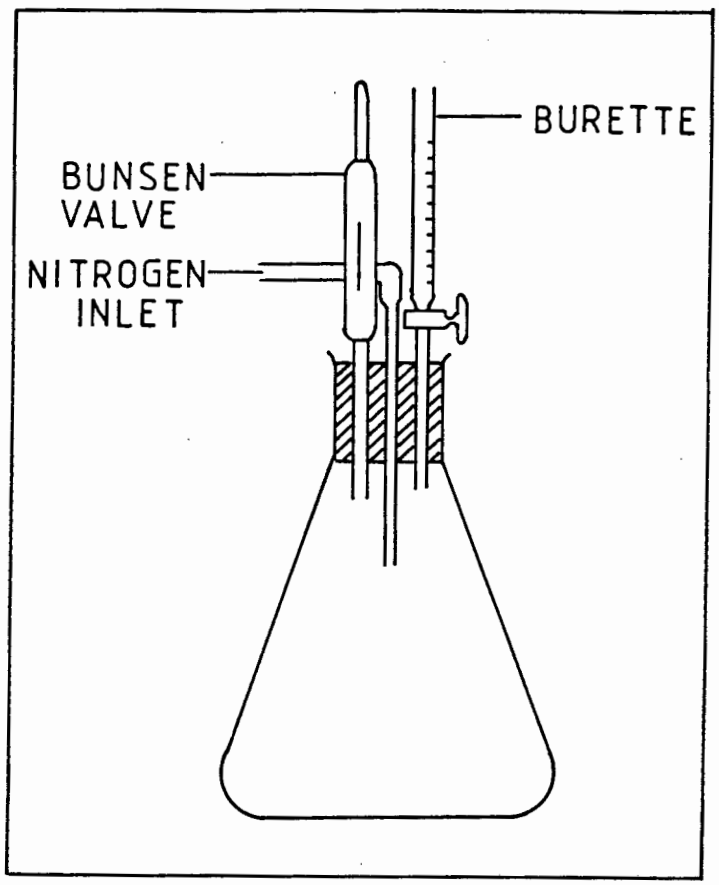


Figure 7.1 Flask with adapted bung for titrations under nitrogen.

During the addition of the potassium iodate both the organic and aqueous phases underwent a number of colour changes. The aqueous phase became reddish-brown and the chloroform layer violet, after approximately 70% of the required iodate solution had been added. As the titration progressed with the dropwise addition of the potassium iodate so the violet colour in the organic phase began to disappear, provided the contents of the flask were agitated vigourously. The end-point is marked by the disappearance of the last trace of violet colour from the chloroform.

7.8 The Distillation of Tin

With the apparatus shown in Figure 7.2, we adapted the procedure of Lehmann[44] to distill tin from a matrix containing dissolved foam, platinum and tin.

50mg of polyurethane foam was placed in flask A containing boiling chips and 10ml of nitric acid. Heat was applied until the foam dissolved ($105^{\circ} \pm 5^{\circ}C$). This solution was allowed to cool and 10mg of tin and platinum were added. Following this 25ml of a 1:1 H_2SO_4 solution was mixed with the contents of flask A and heat was re-applied. At a temperature of $160^{\circ}C$, the dropwise addition of the first in a series of 3 acid mixtures began. The first acid mixture contained 6ml concentrated HBr and 18ml concentrated HCl, the second was composed of 30ml H_2O, 4ml concentrated HBr and 12ml concentrated HCl and the third mixture was identical to the first. The temperature during the addition of these acid mixtures was maintained at $160^{\circ}C$.

In order to achieve quantitative tin distillation we had to raise the temperature of the heating mantle to $235^{\circ}C$ after the acid mixtures had been added. At this temperature the solution became murky and contained a precipitate on cooling. A 10ml quantity of aqua regia added to this stage returned the contents of the flask to its former transparent state.

Solutions in both flasks A and B were suitably diluted and analysed by atomic absorption spectroscopy. Care was taken to match samples and standards for the analysis.

7.9 Apparatus and Procedure used in Cobalt Study

Air bubbles within the polyurethane foam present two problems.

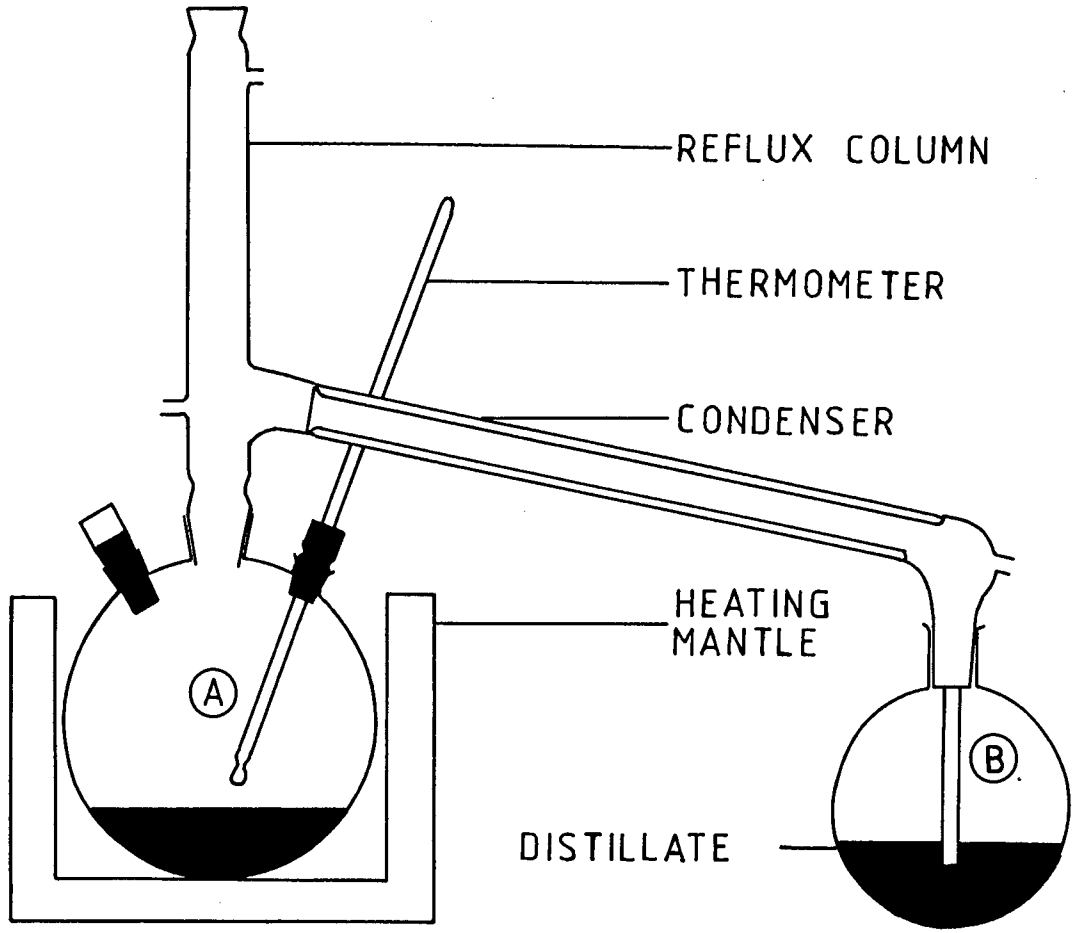


FIGURE 7.2 The Distillation apparatus used to separate platinum from tin.

Firstly, they act as a barrier between the solution and foam and this decreases contact between the two. Secondly, because analysis of cobalt is done by ultraviolet-visible spectrophotometry any bubbles within the cuvette cause a scattering of light.

In order to remove air from the polyurethane, a foam cell illustrated in Figure 7.3 was constructed. The polymer in the foam compartment is compressed by the piston, but as solution is pumped through the system pressure causes the piston to move backwards. The braking mechanism restricts the movement of the piston. This model after some modification eventually reduced the air bubble problem.

Unfortunately after prolonged use the ethanol caused cracking in the perspex foam cell. To construct the same model out of glass would have been extremely difficult and so another system was devised and is shown in Figure 7.4. The model in Figure 7.4 proved to be as effective and more convenient than the one shown in Figure 7.3. For the system shown in Figure 7.4 the foam was simply added to the thermostated bulk solution and the sintered glass tube prevented pieces of the polyurethane foam from passing through the cuvette.

7.10 Apparatus and Procedure used in the Platinum Study

The apparatus shown in Figure 7.5 was used to gather data on the rates of platinum sorption by the polyurethane foam. The foam cell is water jacketed and has an extraction portal for samples to be collected for analysis by AAS. The inverted funnel inside the foam cell provides greater suction to transport small blocks of foam through the tube. The foam is regularly compressed within the tube as it passes between the rollers of the peristaltic pump head. The thermometer is placed in the bulk solution so that temperatures can be carefully monitored and the

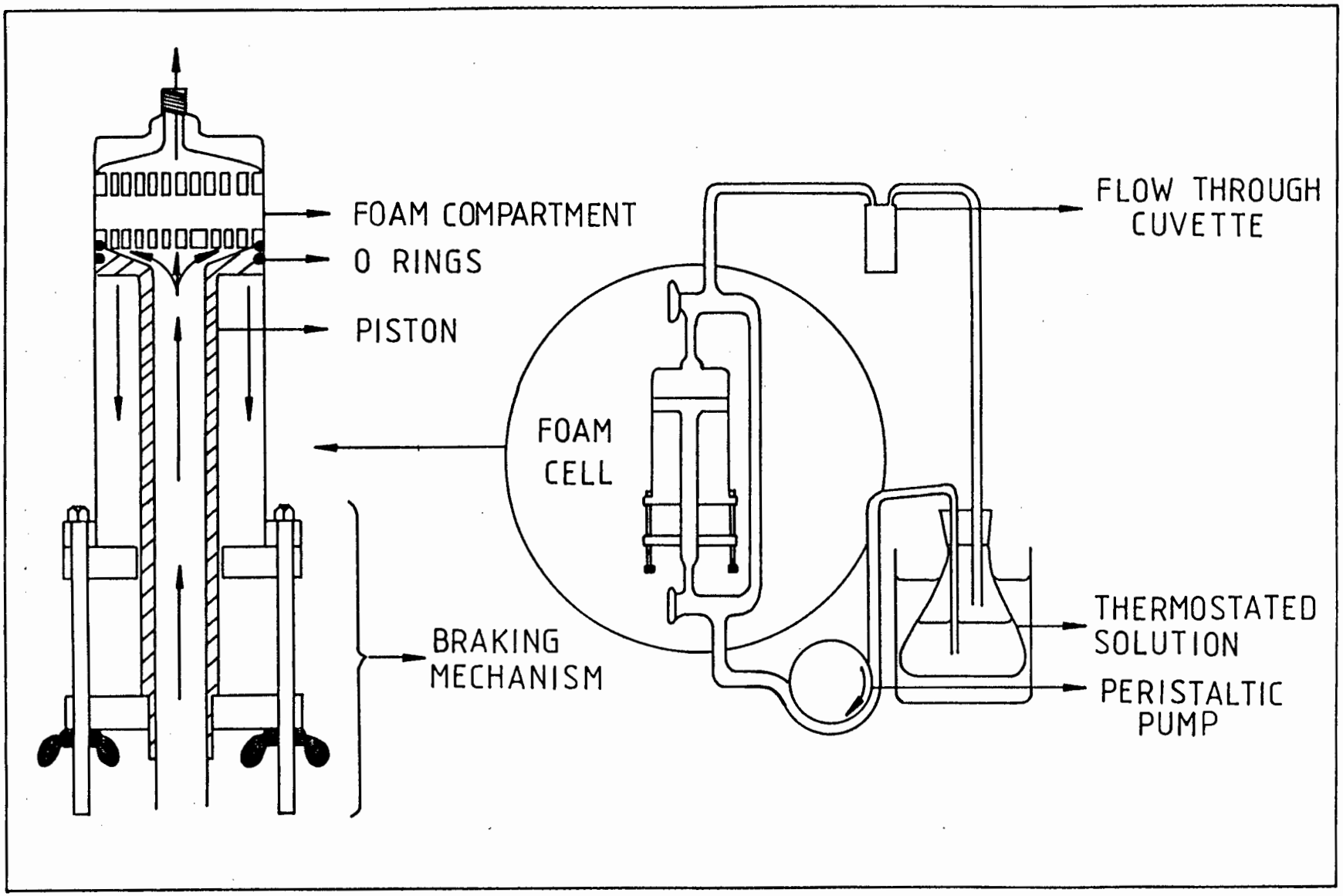


FIGURE 7.3 The experimental apparatus used initially in the Cobalt study

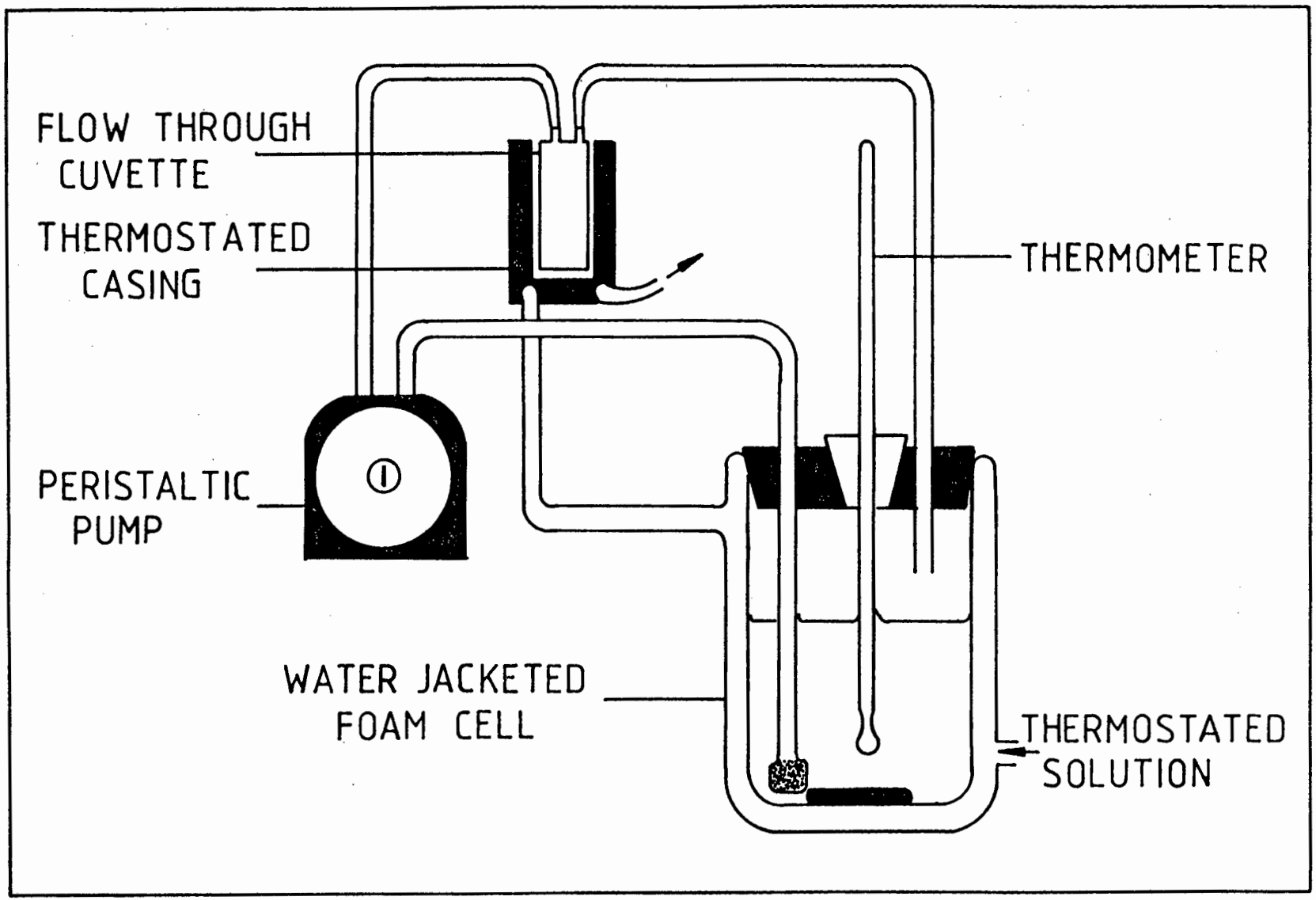


FIGURE 7.4 The experimental apparatus used in the Cobalt study

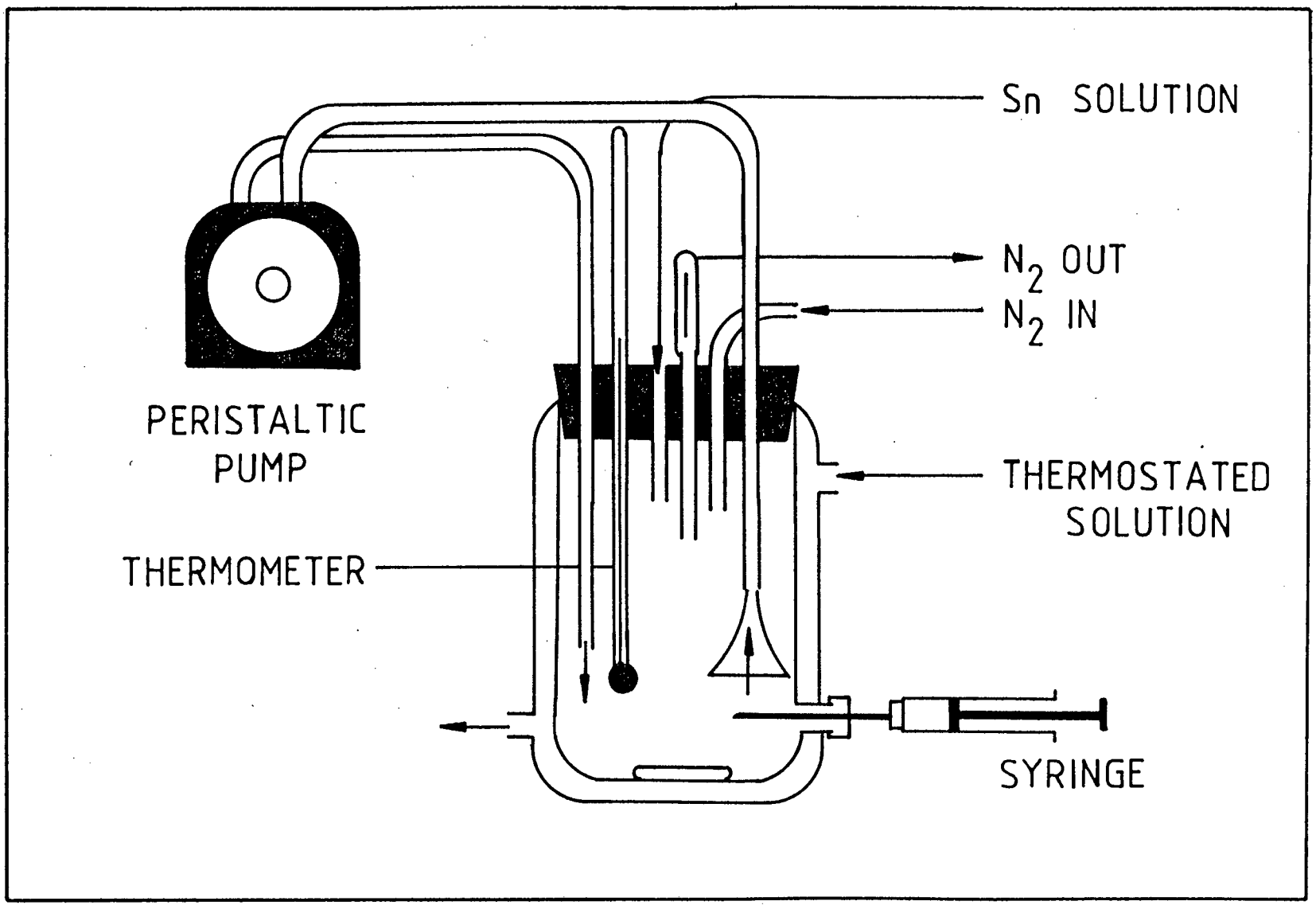


FIGURE 7.5 The experimental apparatus used to study the rates of Platinum Sorption by the Foam

magnetic stirrer ensures that foam and solution are continually mixed.

Although the apparatus discussed above, worked efficiently and served its purpose well, the procedure was too time consuming. It was therefore substituted by the apparatus shown in Figure 7.6. Here the shaker arm provides the necessary mixing of foam and solution. The thermostated water bath serves adequately to maintain solution temperatures at their required levels.

For each experiment, using the apparatus shown in Figure 7.6, two samples were taken. The first sample was withdrawn from the system before the foam was added and the second was taken when the foam and the aqueous phase were at equilibrium. In all cases the solutions were kept under nitrogen.

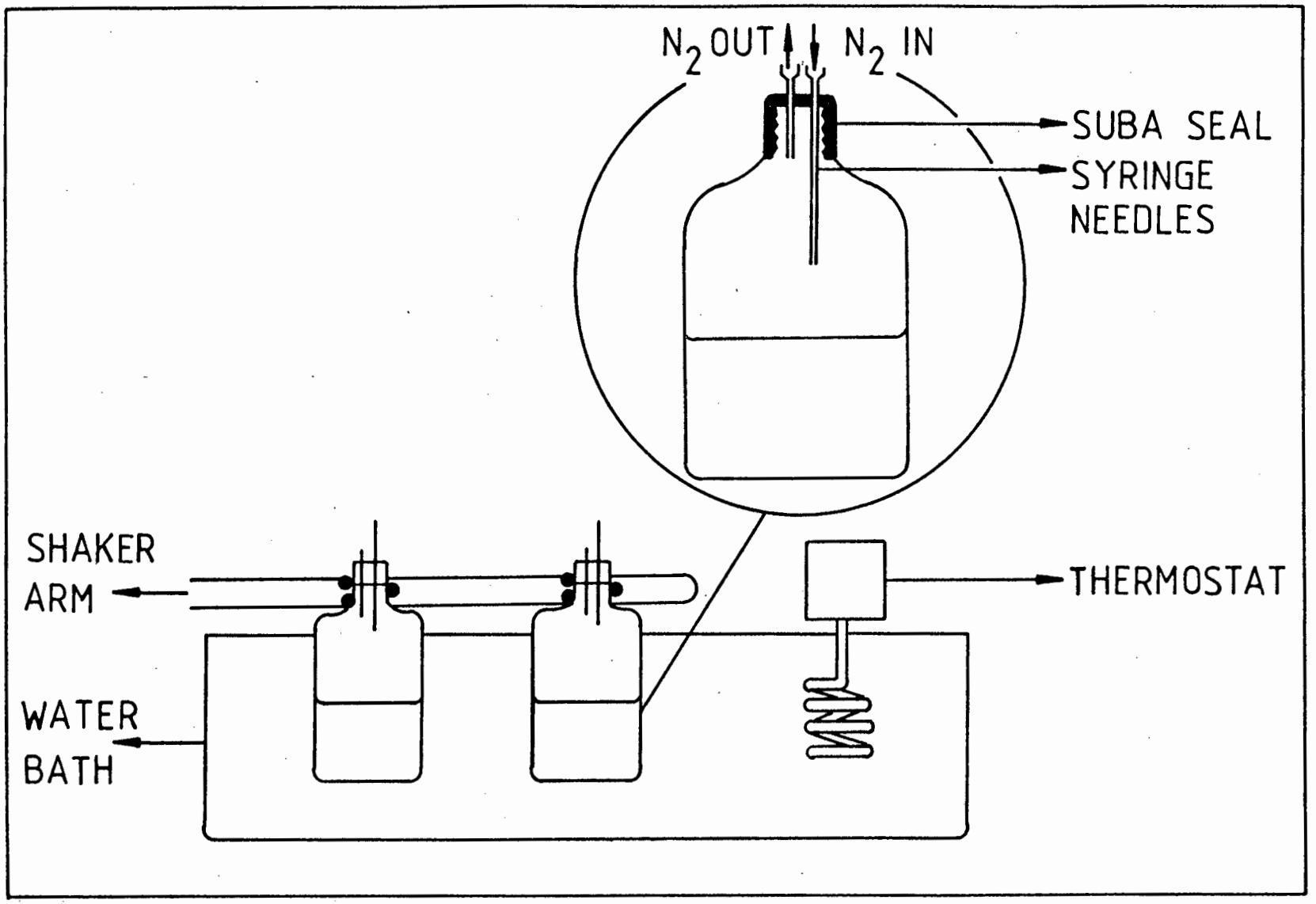


FIGURE 7.6 The experimental apparatus used for non-kinetic work in the Platinum study

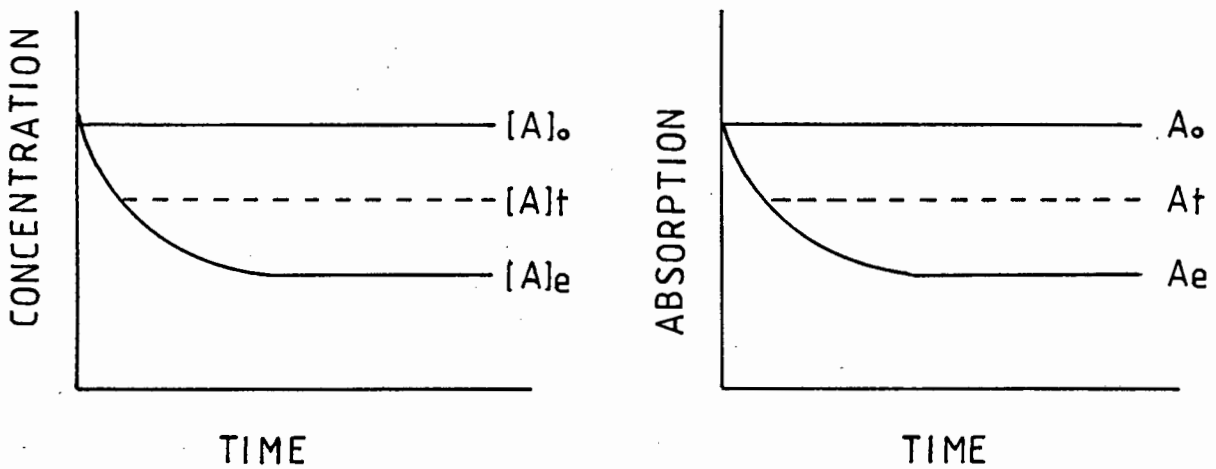
APPENDIX

APPENDIX 1

DERIVATION OF EQUATION 2

$$\text{Ln}\ \frac{Ae}{At-Ae} = kt \quad \text{is derived from} \quad \text{Ln}\ \frac{[A]o}{[A]t} = kt$$

The diagrams below represent a typical UV-VIS spectrophotometric time scan at a constant wavelength (λ_{max} = 618 nm), of a $Co(NCS)_4^{2-}$ solution from which the cobalt anion is being extracted by a quantity of polyurethane foam.



A constant wavelength time scan of a cobalt solution containing polyurethane foam.

[A]o = initial Concentration Ao = initial Absorbance

[A]t = Concentration at time t At = Absorbance at time t

[A]e = Concentration at equilibrium Ae = Absorbance at equilibrium

Since $[A]o \propto Ae$

and $[A]t \propto At - Ae$

So the equation $\text{Ln}\ \frac{[A]o}{[A]t} = kt$ may be rearranged

to $\text{Ln}\ \frac{Ae}{At - Ae} = kt$

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